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Porewater profiles in the Eco Wasp ecosystem model

A.G. Brinkman & J.P.C. Smit

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Errata.

Page	Line	Error	Should be
10	Figure 2 caption	.. processen ..	.. processes ..
		.. directen ..	.. directed ..
11	line 8	.. NO_{3-} ..	.. NO_3^- ..
		.. SO^{2-}_4 ..	.. SO_4^{2-} ..
15	below eq.1 (twice)	.. $(molm^{-3}$	.. $(mol \cdot m^{-3}$
16	1 line below eq.3	.. $\sigma^{i,j}$ ..	.. $\alpha_{i,j}$ ..
20	4 lines below eq.29	.. a-parameters ..	.. α-parameters ..
	7 lines below eq.29	.. correct a_k's ..	.. correct α_k's ..
22	1 line below eq.38	.. conditions ..	.. condition ..
23	3 lines below eq.48	.. as i done ..	.. as is done ..
25	sect. 3.1, line 2	.. ion act ..	.. ion acts ..
26	line 17	.. general will ..	.. generally will ..
	line 36	(Table 1, page 51)	(Table 2, page 49)
30	Figure 7	all equation numbers	should be 1 lower
32	eq.57	no eq. number	(57)
	1 line below eq.57	"	If
	Sect. 3.3, line 1	..(35),(64),(44)-(46)	..(35),(44)-(46)
33	2 lines below eq.60	.. coefficients and ..	.. coefficients β and ..
37	Fig.14 caption	Iteraion .. oxyge ..	Iteration .. oxygen ..
43	eq.67	R_1 should be multiplied by the porosity μ because R_1 concerns the pore water volume and C_{ads} concerns the system volume	
45	section 4.3.4 line 2	H_2PO_{4-}	$H_2PO_4^-$
		NH_4+	NH_4^+
47	Sect 4.3.6 line 9	(Fig.20)	(Fig.23)
48	line 2	NO_{3-}	NO_3^-

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This report is the third document on the development of the EcoWasp ecosystem model for tidal systems

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CONTENTS

PREFACE

In 1988, the Institute for Forestry and Nature Research (IBN) (then the Research Institute for Nature Management (RIN)) and the Netherlands Institute for Sea Research (NIOZ) agreed upon the further development of an ecosystem model describing key processes in tidal systems such as the Dutch Wadden Sea. This agreement was part of a broader cooperation within the framework of the BEON modelling group, the official modelling platform of the major marine research and management institutions in the Netherlands. An important goal was that the model should play an important role in tidal system process studies and in answering Wadden Sea management questions.

In 1990, cooperation between IBN, NIOZ and a number of other institutes from Denmark, Germany and The Netherlands was established within the framework of the Marine Science and Technology program (MAST) of the European Committee. This project(MAST-project 0026) was called Wadden Sea Project (WASP) and aimed at the investigation of the link between descriptions of physical, chemical and biological processes in a Wadden Sea system. In WASP, NIOZ and IBN were responsible for the development of the ecosystem model. To distinguish from the former NIOZ model EMOWAD, and to express the relation with the EC-project, the new model is called EcoWasp.

Basic process descriptions were mainly found in the EMOWAD model (Baretta & Ruardij, 1988; EON, 1988-a, 1988-b) and the freshwater model TmSim, developed at the Twente University of Technology (Brinkman, 1989).

During the EcoWasp development, most attention has been paid to process descriptions concerning the calculation of pore water profiles plus sediment/water interactions and to zooplankton- and zoobenthos dynamics. In EcoWasp, many of the EMOWAD description on these two subjects are completely renewed.

In this report, the computation of pore water profiles and sediment/water fluxes is documented. Concepts, reaction descriptions and algorithms are described and tested. The algorithms are implemented in the EcoWasp ecosystem software package. A review on the EcoWasp model is given by Brinkman and Smit (1993).

The authors wish to thank Dr. Ir. W. van Raaphorst (NIOZ) for his very valuable comments.

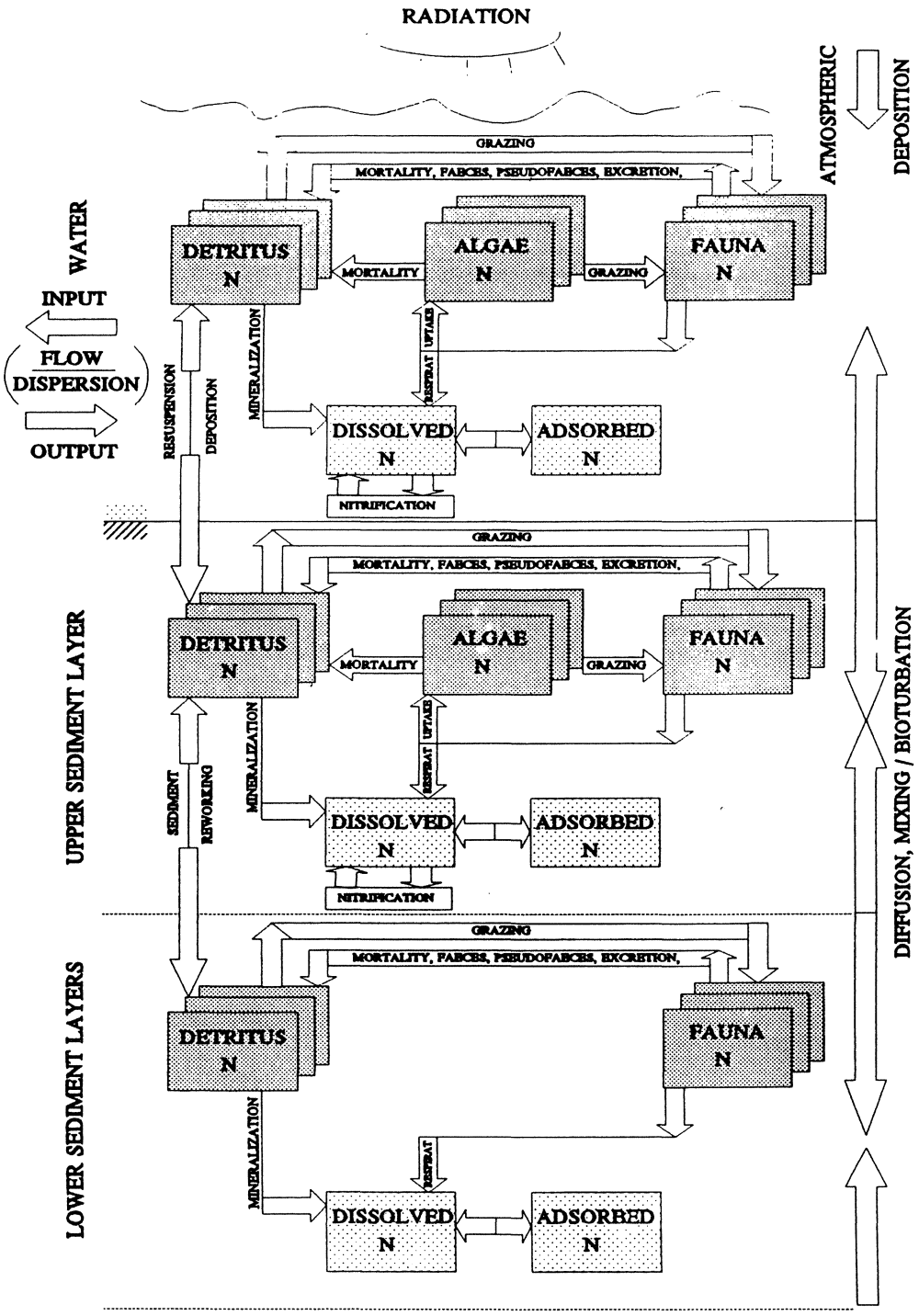


Figure 1. General outline of EcoWasp processes and flows, using Nitrogen (N) as an example element.

1. INTRODUCTION

1.1. General

Descriptions of biological processes and of sediment/water interactions form the main part of the EcoWasp ecosystem model. In this report, the pore water profile computation and the sediment/water exchange are outlined. It should be regarded as the technical reference of EcoWasp, concerning sedimentary pore water processes. The reader is also referred to the 'Structure of the EcoWasp ecosystem simulation model and its application to the Dutch Wadden Sea' (Brinkman and Smit, 1993) which gives a general overview of the model.

In EcoWasp, the system is divided horizontally into a number of compartments and vertically into a number of layers. The uppermost layer is the water phase, all the others are located in the sediment. In each of these layers all the modelled biological and chemical processes are computed. Vertical transport mainly occurs through diffusion, sedimentation/resuspension (solids) and through biological activities (bioturbation and bioirrigation). Horizontal transport only occurs in the water phase through advection and dispersion.

In Fig.1 an overview is given of the modelled processes and flows of matter. As an example, nitrogen (N) is used since it is part of most of the implemented processes. The sediment part is presented as simply as possible. In reality, the model is more complicated, especially regarding the number of layers.

Three main types of biological processes are modelled in EcoWasp: primary production, biochemical degradation and fauna dynamics. These processes occur in the overlying water and in the sediment. In the sediment they result in production or consumption rates of dissolved components such as phosphate and oxygen.

Macro- and meiofauna may take up particles (which may be algae, detrital matter, other animals and inorganic matter) and utilize the organic compounds partly for their growth. Another part is excreted as faeces or rejected as pseudofaeces. As a result of their food collection and faeces production, benthic animals may actively transport solids from the overlying water to the sediment (most times the sediment surface) or from one sediment layer to another (Boudreau, 1986-a, 1986-b).

An important non-biological process affecting benthic nutrient cycling is the adsorption or desorption of ions onto or from solids. Especially silicate and phosphate show strong sorption onto metal-oxihydroxides. Sorption of ammonia and of divalent cations generally is weaker, but may certainly be substantial.

This report contains four main parts: 1: the diffusion-reaction equation that is applied (section 2); 2: implemented algorithms (section 3); 3: reactions that take place in the sediment and in the pore water, and that are the driving forces for the rates of change (section 4); 4: corrections and tests (section 6). In section 5, routines as they are used in EcoWasp are summarized.

1.2. The multilayer concept

The sediment is divided into a number of layers, each having its own characteristics such as thickness, porosity, solids composition and temperature.

In these sediment layers, a number of processes takes place that influence pore water components (Fig.2):

1- diffusion
2- advection
3- adsorption/desorption
4- precipitation/dissolution
5- production/consumption by microorganisms and reactions such as nitrification

In EcoWasp, mainly diffusion, adsorption/desorption and production/consumption are considered.

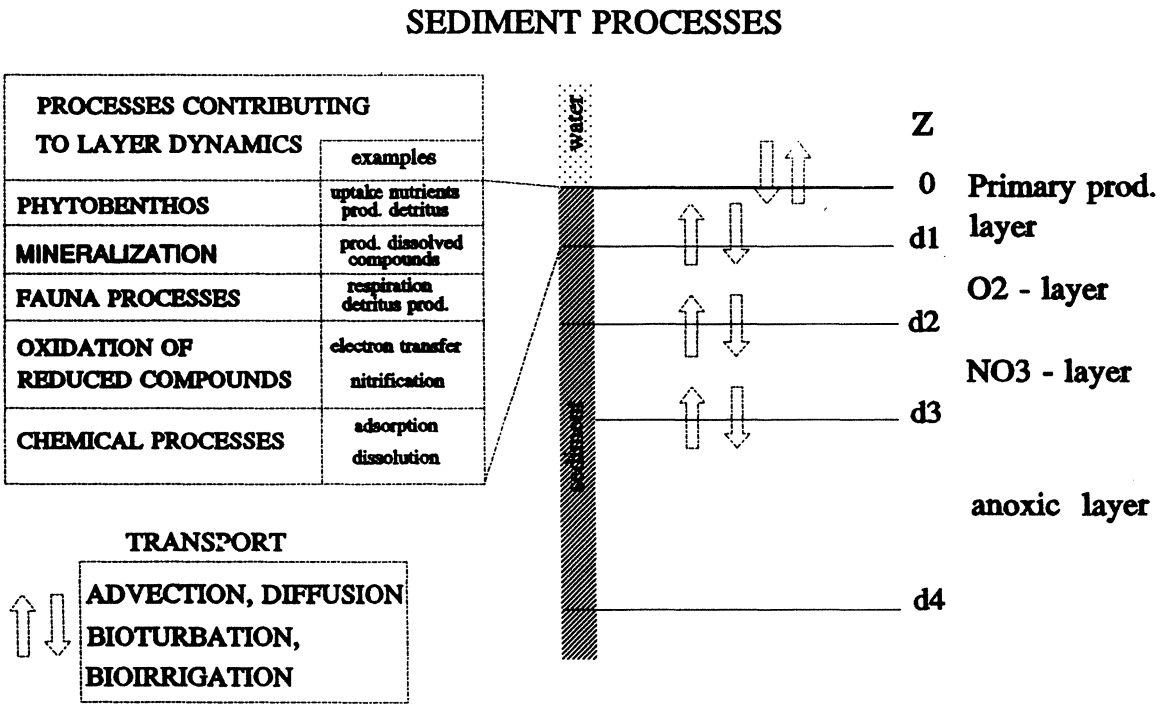


Figure 2. Sediment processen in EcoWasp affecting solid and pore water composition. The positive Z-axis is directen downward.

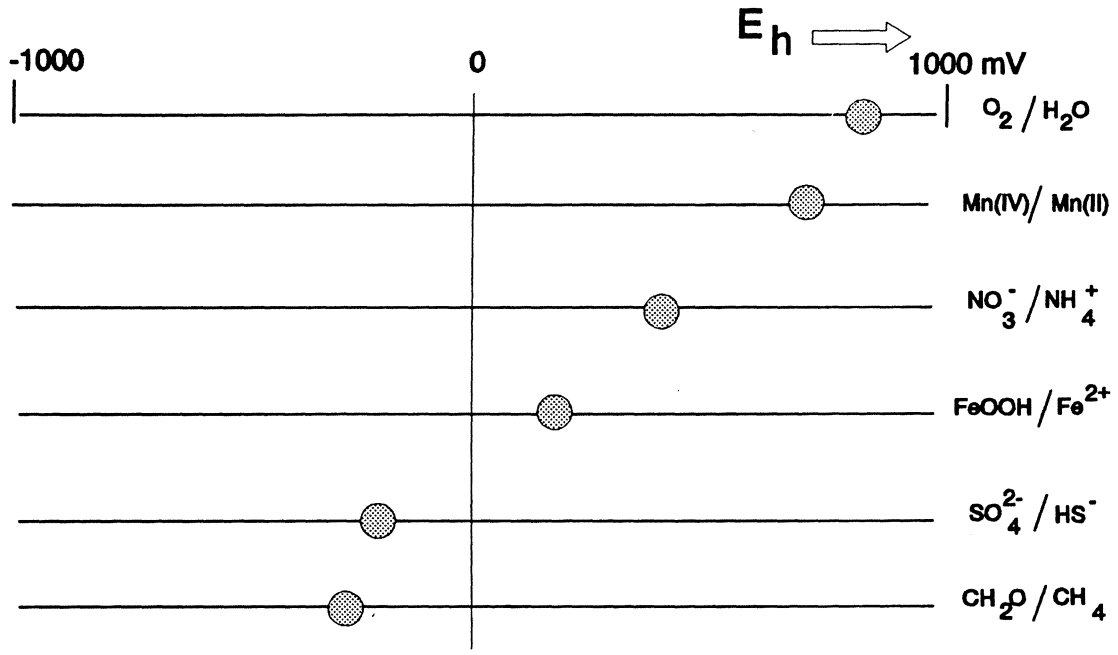


Figure 3. Normal electron acceptor sequence in natural systems under natural pH conditions.

The pore water composition is computed from the steady state solution of diffusion-reaction equations (section 2). The assumption of a steady state implies that the time needed for the establishment of porewater profiles is much less then the size of the integration step used. Corrections to this assumptions are discussed in section 5.

A process that determines the sediment characteristic for a large part is the oxidation of organic matter by bacteria. This oxidation is accompanied by a reduction of inorganic components such as O_2, Mn-IV, NO_3_ , Fe-III and SO^{2-}_4(Bender & Heggie, 1984; Froelich et al, 1979). Oxygen, nitrate and sulphate diffuse from the overlying waters into the sediment; additionally, nitrate also may be produced by ammonia oxidizing bacteria. When oxygen is absent, Mn(IV) may be reduced to Mn(II), and, in addition, nitrate will be reduced to N_2 At greater depths, in absence of oxygen and nitrate, reduction of iron(III), sulphate, and organic material itself, occurs. The Fe(III) reduction produces Fe(II), sulphate reduction gives sulphides and sulphur. When organic material is reduced, methane and a number of organic acids (acetic acid, propionic acid, etc.) are formed. Under sulphate reduction or fermentation conditions, the organic material is only partly transformed into the inorganic end-products. The common electron acceptor order in natural systems is shown in Fig.3 (see e.g. Stumm and Morgan, 1970).

The depth at which oxygen is depleted is determined by the oxygen consumption rate and the oxygen influx. The influx of nitrate and the nitrate production rate through nitrification on one hand, and the nitrate consumption rate (denitrification) deeper in the sediment on the other hand, determine the depth at which a nitrate depletion occurs.

Some characteristics depend on the oxidation state of notably iron. For example, phosphates bind very strongly onto Fe(III)-oxides, but the interactions with Fe(II)-compounds (e.g. Fe(II)-carbonates and -sulphides) are much weaker. This effect makes clear how important it is to have a good estimate of the oxidation/reduction state ('redox condition') at each position in the sediment.

Penetration depths of electron acceptors, as depicted in Fig.2, generally will change from timestep to timestep. These changes give numerical problems (integration errors, or very thin layers that may give problems when consumption by fauna is to be computed). To avoid such problems, we defined a fixed layer system. All the solid characteristics are defined for these fixed layers, and so are the fauna characteristics.

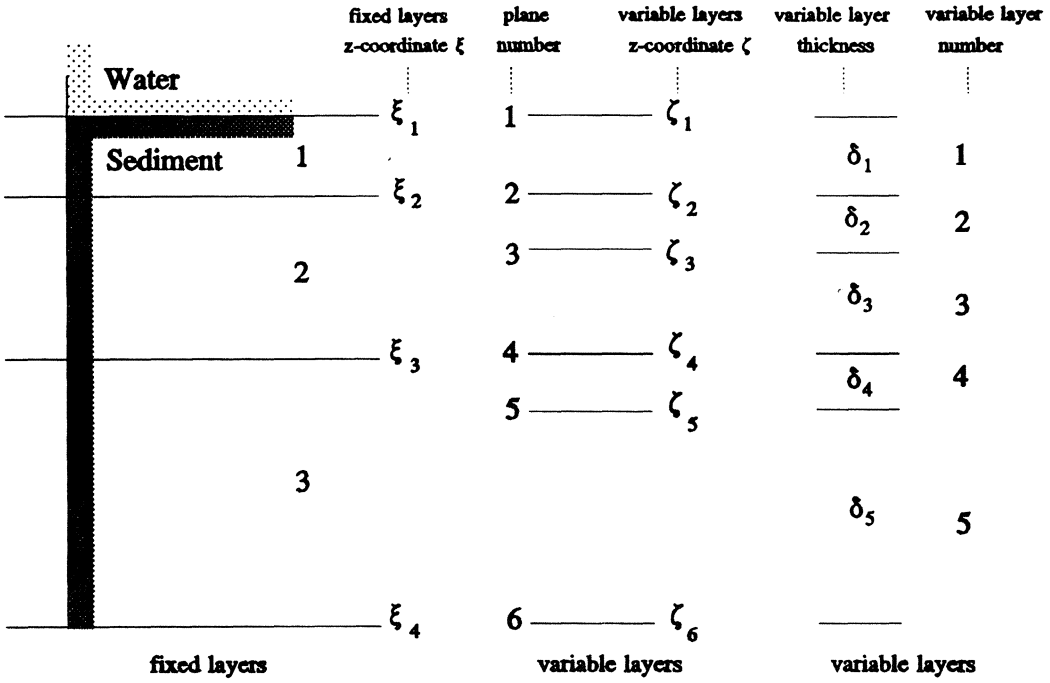


Figure 4. Sediment layer schematization. Fixed layers have to be chosen by the EcoWasp user, the variable layers are computed by EcoWasp during the computation of the benthic processes.

Generally, these fixed layer positions will not coincide with the penetration depths. For the computation, however, it is necessary that the variable layer schematization always fits to the fixed layer system. In EcoWasp, the compu-

tation starts with the fixed layer schematization. Then, using the reaction rates as computed for the given situation, first the oxygen penetration depth is computed, then the nitrate penetration depth, etcetera. Each penetration depth results in a new variable layer. Each time a fixed layer position is passed, this is also considered as a variable layer boundary. Thus, the variable layer boundaries always coincide with fixed layer boundaries, plus some extra boundaries that mark the change from one electron acceptor situation to another. The total number of variable layers is (number of fixed layers + number of electron acceptors (including organic matter) -1). Doing so, the numerical dispersion that would result from a schematization using only variable layers is eliminated. Inside each fixed layer, more than one variable layer may exist, each having their own process characteristics such as the degradation rate of organic matter. Mass budgets are computed for all the variable layers. This implies that during the simulation the situations in these variable layers may diverge. Small changes from timestep to timestep will cause numerical dispersion, but this is restricted to this one fixed layer alone. In Fig.4, the definition of the sediment layer system is depicted completely.

2. THE DIFFUSION-REACTION EQUATION

2.1. Introduction

The general diffusion-reaction equation for pore water reads

$$\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial z^2} - v_z \cdot \frac{\partial C}{\partial z} + R \qquad (\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}) \quad (1)$$

with

D = diffusion coefficient (m^2s^{-1})
v_z = advection velocity (ms^{-1})
z = depth (m)
C = concentration ($molm^{-3}$ pore water)
R = reaction term ($molm^{-3}s^{-1}$ pore water)

R contains all the reaction terms. The form of R determines the solution of eq.(1) (Crank, 1975; Berner, 1980). In most case, R may be zero to second order or even higher, in C. Also, this order can be a real instead of an integer. The diffusion equation is not easily solved when R contains other than zero or first order terms. In EcoWasp, we restricted ourselves to (pseudo-) zero- and first order descriptions. When a reaction rate is *not* zero- or first order in C, these descriptions are *made* zero- or first order by lumping the non zero- or first order part by an adapted rate constant. The consumption of electron acceptors by the mineralization process is made zero order. By doing so, there is a depth at which the concentration of the acceptor becomes zero; this depth can be calculated quite easily. Another possibility would have been to assume a first order reaction. In that case, the acceptor concentration never becomes zero, and the change to another acceptor dominance would have to be defined in terms of a lower concentration limit.

In EcoWasp, steady state is assumed: eq.1's left hand term equals zero. Such an assumption is valid when the time needed to establish a concentration profile is short compared to the timestep used for the simulation computations. The validity of this assumption is checked by Brinkman and Van Raaphorst (1986) for a simple phosphate sediment pore water diffusion where R contained terms that were first and zero order in C. Van Raaphorst et al (1988) found that the time needed for a concentration profile to adapt itself to new conditions in the overlying water is in the order of minutes to hours (10^2 to 10^4 seconds); a typical simulation timestep is one day.

In EcoWasp, we neglected the advection term v_z. Reason for this is that we do not know at all what form v_z has, or what its direction is. Most times, v_z will probably change direction as a result of the tidal movements, and will have a tidally averaged value around zero. Such a transport might better be described by a dispersion term.

Three cases are distinguished in EcoWasp:

1- the reaction term is zero order in C and negative, or at least: negative at large depths. Because of this consumption, depletion at large depths occurs.
2- the reaction term is zero order in C and positive : there is production of the component.
3- (part of) the reaction terms are first order in C. Zero order terms may appear also.

The solution of the diffusion equation is different for each of the above mentioned three cases, which will be treated in the next sections.

2.2. The reaction term R is zero order in C

2.2.1. General

Neglecting advection, assuming steady state,and setting $R = R_0$ for all z, the diffusion equation reads

$$0 = D \cdot \frac{\partial^2 C}{\partial z^2} + R_0 \qquad (\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}) \quad (2)$$

The general solution of eq.(2) for each layer j is

$$C_{j,z} = \alpha_{1,j} \cdot z^2 + \alpha_{2,j} \cdot z + \alpha_{3,j} \qquad (\text{mol} \cdot \text{m}^{-3}) \quad (3)$$

The integration constants $\alpha^{i,j}$ (i=1..3; j=layer number) depend on the boundary conditions of each layer. It suits very well to write the solution for each layer using adapted coordinates:

$$C_{j,z} = \alpha_{1,j} \cdot (z-\zeta_j)^2 + \alpha_{2,j} \cdot (z-\zeta_j) + \alpha_{3,j} \qquad (\text{mol} \cdot \text{m}^{-3}) \quad (4)$$

with

ζ_j = z-coordinate of plane j between layer (j-1) and layer j

Substituting

$$Z_j = z-\zeta_j \qquad (\text{m}) \quad (5)$$

gives more readable equations.

The first boundary conditions concern the concentration equality at each plane j:

$$C_{j|z_j=0} = C_{j-1|z_{j-1}=\delta_{j-1}} \qquad (\text{mol} \cdot \text{m}^{-3}) \quad (6)$$

with δ_{j-1} is the thickness of layer j-1.

For the first layer (j = 1), the concentration at z = 0 ($Z_1 = 0$) is assumed to be equal to the concentration in the water column:

$$C_{1_{|z_1=0}} = C_0 \qquad (\text{mol} \cdot \text{m}^{-3}) \quad (7)$$

This is because it is assumed that the resistance against the exchange of dissolved matter lies in the sediment porewater, and not in the water just above the sediment surface.

The second condition concerns the fluxes through plane j. The flux is calculated after Fick's first law:

$$J_j = -D_j \cdot \mu_j \frac{\partial C_j}{\partial Z} \qquad (\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}) \quad (8)$$

in which μ_j is the layer j porosity (-), and D_j is the effective diffusion coefficient, which equals

$$D_j = D_0 \cdot (tortuosity_j)^{-2} \qquad (\text{m}^2 \cdot \text{s}^{-1}) \quad (9)$$

where D_0 is the molecular diffusion coefficient ($m^2.s^{-1}$). Values for D_0 can be found in common tables.

At both sides of a plane, these fluxes should be equal. So, the second condition reads:

$$D_{j-1} \cdot \mu_{j-1} \cdot \frac{\partial C_{j-1}}{\partial Z_{j-1}}|_{Z_{j-1}=\delta_{j-1}} = D_j \cdot \mu_j \cdot \frac{\partial C_j}{\partial Z_j}|_{Z_j=0} \qquad (\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}) \quad (10)$$

Following eq.(4), this gives

$$D_{j-1} \cdot \mu_{j-1} \cdot (2 \cdot \alpha_{1,j-1} \cdot \delta_{j-1} + \alpha_{2,j-1}) = D_j \cdot \mu_j \cdot \alpha_{2,j} \qquad (\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}) \quad (11)$$

This second condition has a different form for the 'final' plane (m + 1) across which we assume that there is no diffusive transport. **So, we assume a certain sediment system depth.** So, when the flux through this final plane (m + 1) equals zero, the third condition reads

$$0 = \frac{\partial C_m}{\partial Z}|_{Z_m=\delta_m} \qquad (\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}) \quad (12)$$

and, consequently:

$$0 = 2 \cdot \alpha_{1,m} \cdot \delta_m + \alpha_{2,m} \qquad (\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}) \quad (13)$$

We now have two conditions for each layer: a concentration continuity condition and a flux continuity condition.

Because of steady state, the rate at which a component is produced in any layer j should equal the net flux out of that layer. Thus

$$J_{j+1} = R_{0,j} \cdot \delta_j + J_j \qquad (\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}) \quad \textbf{(14)}$$

or

$$-D_{j+1} \cdot \mu_{j+1} \cdot \frac{\partial C_{j+1}}{\partial Z}\Big|_{Z_{j+1}=0} = R_{0,j} \cdot \delta_j - D_j \cdot \mu_j \cdot \frac{\partial C_j}{\partial Z}\Big|_{Z_j=0} \qquad (\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}) \quad \textbf{(15)}$$

J_{j+1} is the outflux from layer j to layer (j + 1), J_j is the influx to layer j from layer (j-1). Eq.(15) can be written as

$$-D_{j+1} \cdot \mu_{j+1} \cdot \alpha_{2,j+1} = R_{0,j} \cdot \delta_j - D_j \cdot \mu_j \cdot \alpha_{2,j} \qquad (\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}) \quad \textbf{(16)}$$

By this, for each layer the three necessary conditions are formulated.

These equations hold for both R_0 possibilities: $R_0 > 0$ and $R_0 < 0$. When $R_0 < 0$ (consumption of the C), there will be some depth at which C_z becomes zero. In section 2.2.2 the situation where $R_0 > 0$ will be discussed. In section 2.2.3 the equation with $R_0 < 0$ will be solved.

2.2.2. Zero order production

Expressions for the integrations constants $\alpha_{i,j}$, ($i = 1..3, j = 1..m$) are needed now. From eq.(16) it follows that for $j = 1..(m-1)$

$$\alpha_{2,j} = \frac{R_{0,j} \cdot \delta_j + D_{j+1} \cdot \mu_{j+1} \cdot \alpha_{2,j+1}}{D_j \cdot \mu_j} \qquad (\text{mol} \cdot \text{m}^{-4}) \quad \textbf{(17)}$$

and, for the fifth layer m (the left hand term in eq.(16) equals 0):

$$\alpha_{2,m} = \frac{R_{0,m} \cdot \delta_m}{D_m \cdot \mu_m}$$

Applying eqs. (17) and (18) for all layers, it can be seen that the general expression for $\alpha_{2,j}$ becomes:

$$\alpha_{2,j} = \frac{\sum_{i=j}^{m} R_{0,i} \cdot \delta_i}{D_j \cdot \mu_j} \qquad (\text{mol} \cdot \text{m}^{-4}) \quad \textbf{(19)}$$

For $\alpha_{1,j}$, the flux continuity condition (eqs.(10) and (11)) gives

$$\alpha_{1,j} = \frac{1}{2 \cdot \delta_j} \cdot \left(\frac{D_{j+1} \cdot \mu_{j+1}}{D_j \cdot \mu_j} \cdot \alpha_{2,j+1} - \alpha_{2,j} \right) \quad (\text{mol} \cdot \text{m}^{-5}) \quad (20)$$

for j = 1..(m-1), and for j = m it follows:

$$\alpha_{1,m} = -\frac{1}{2 \cdot \delta_m} \cdot \alpha_{2,m} \quad (\text{mol} \cdot \text{m}^{-5}) \quad (21)$$

According to eq.(4), for Z = 0, it follows for each layer j that

$$C_{j,Z=0} = \alpha_{3,j} \quad (\text{mol} \cdot \text{m}^{-3}) \quad (22)$$

and, for $Z = \delta_{j-1}$ for each layer (j-1)

$$C_{j-1,Z=\delta_{j-1}} = \alpha_{1,j-1} \cdot \delta_{j-1}^2 + \alpha_{2,j-1} \cdot \delta_{j-1} + \alpha_{3,j-1} \quad (\text{mol} \cdot \text{m}^{-3}) \quad (23)$$

So, from the concentration continuity condition $\alpha_{3,j}$ reads

$$\alpha_{3,j} = \alpha_{1,j-1} \cdot \delta_{j-1}^2 + \alpha_{2,j-1} \cdot \delta_{j-1} + \alpha_{3,j-1} \quad (\text{mol} \cdot \text{m}^{-3}) \quad (24)$$

while, for j = 1, $\alpha_{3,1}$ is

$$\alpha_{3,1} = C_0 \quad (\text{mol} \cdot \text{m}^{-3}) \quad (25)$$

The equations (24) and (25) are solved starting with the calculation for layer 1, and ending with layer m.

The expressions for all integration constants are summarized in Table 1.

2.2.3. Zero order consumption

When a dissolved component is consumed, its concentration becomes zero at a certain depth δ_k. The equations that describe the integration constants $\alpha_{i,j}$ are still valid; the only difference is that the depth δ_κ is not known and has to be calculated too. Consequently, one extra equation is needed for the final layer.

The flux continuity condition and the concentration continuity condition at Z = 0 are both still valid. The only extra condition needed is that at $Z = \delta_k$ $C_{z,k} = 0$:

$$C_{\delta_k} = \alpha_{1,k} \cdot \delta_k^2 + \alpha_{2,k} \cdot \delta_k + \alpha_{3,k} = 0 \quad (\text{mol} \cdot \text{m}^{-3}) \quad (26)$$

Eq.(21) gives $\alpha_{1,k}$. Eq.(18) gives $\alpha_{2,k}$. Eq.(22) gives $\alpha_{3,k}$. After substitution of these equation in eq.26 it follows that

$$0 = -\frac{R_{0,k}}{2 \cdot D_k \cdot \mu_k} \cdot \delta_k^2 + \frac{R_{0,k}}{D_k \cdot \mu_k} \cdot \delta_k^2 + C_{k,0} \qquad (\text{mol} \cdot \text{m}^{-3}) \quad (27)$$

or

$$0 = \frac{R_{0,k}}{2 \cdot D_k \cdot \mu_k} \cdot \delta_k^2 + C_{k,0} \qquad (\text{mol} \cdot \text{m}^{-3}) \quad (28)$$

and it gives for δ_k:

$$\delta_k = \sqrt{\frac{-2 \cdot C_{k,0} \cdot D_k \cdot \mu_k}{R_{0,k}}} \qquad (\text{m}) \quad (29)$$

The concentration of the consumed component at Z = 0 of this final layer k is $C_{k,0}$. This concentration is not really known, but it will be the estimator of the iterative procedure necessary for the calculation of δ_k. C_k is given some starting value, δ_j is calculated, and subsequently all the other a –parameters result from the standard equations. Using these parameters, C_k is calculated again, and compared to the previous estimate of C_k. A simple Newton iteration procedure is used to calculate the correct C_k-value (and the correct a_k's and δ_k).

The algorithm for the calculation of all the δ_k's is described in section 3.

2.3. The reaction term is (also) first order in C

2.3.1. First order general solution

Assuming steady state, equation 1 is rewritten as

$$0 = D \cdot \frac{\partial^2 C}{\partial z^2} - v_z \cdot \frac{\partial C}{\partial z} + R_1 + R_0 \qquad (\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}) \quad (30)$$

where R_1 is the first order reaction term, and R_0 the zero order production (or consumption) term (mol.m^{-3} (pore water).s^{-1}). It is not important whether R_0 appears in the equation or not; the solution of the diffusion equation will be valid in both cases.

The first order term R_1 reads

$$R_{1,j} = -k_{1,j} \cdot C_j \qquad (\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}) \quad (31)$$

in the case of a simple first order decay, or

$$R_{1,j} = -k_{1,j} \cdot (C_j - C_{eq,j}) \qquad (\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}) \quad (32)$$

in the case of an adsorption/desorption reaction where an equilibrium concentration $C_{eq,j}$ is to be reached. The factor $k_{1,j}$ denotes the first order rate constant (s^{-1}), that may be related to relevant sediment characteristics such as adsorption capacity.

Note that C is *not* in equilibrium with the adsorbed phase ($C_j \# C_{eq,j}$); after each profile calculation, the adsorption has to be calculated. The necessary adsorption equilibrium calculation procedure is reported separately.

The diffusion equation (30) now reads (again, $v_z = 0$)

$$0 = D \cdot \frac{\partial^2 C}{\partial z^2} - k_1 \cdot (C - C_{eq}) + R_0 \qquad (\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}) \quad (33)$$

The general solution of eq.(33) is, for each layer j :

$$C_{z,j} = E_j + A_j \cdot \exp(\lambda_{1,j} \cdot z) + B_j \cdot \exp(\lambda_{2,j} \cdot z) \qquad (\text{mol} \cdot \text{m}^{-3}) \quad (34)$$

with

$$E_j = \frac{R_{0,j}}{k_{1,j}} + C_{eq,j} \qquad (\text{mol} \cdot \text{m}^{-3}) \quad (35)$$

where C_{eq} and $k_{1,j}$ are according to the definitions given above, for each layer j, and

$$\lambda_1 = -\sqrt{\frac{k_{1,j}}{D_j}} \qquad (\text{m}^{-1}) \quad (36)$$

and

$$\lambda_2 = \sqrt{\frac{k_{2,j}}{D_j}} \qquad (\text{m}^{-1}) \quad (37)$$

λ_1 is negative, and λ_2 is positive.

2.3.2. Description of integration constants

A number of boundary and continuity conditions should be met:

1- $z = 0$: $C_z = C_0$ = Concentration in overlying water
2- concentration at the planes should be the same in both adjacent layers (concentration continuity condition);
3- $z = \infty$: C_z = finite
3- fluxes though the planes should be the same at both sides of the planes (flux continuity condition).

The $Z_j = z - \zeta_j$ coordinates as introduced above (section 2.2, eq.5) are used.

The first condition gives

$$C_{1,0} = C_0 \qquad (\text{mol} \cdot \text{m}^{-3}) \quad (38)$$

The second conditions gives:

$$C_j(\delta_j) = C_{j+1}(0) \qquad (\text{mol} \cdot \text{m}^{-3}) \quad (39)$$

and, consequently

$$C_{eq_j} + \frac{R_{0j}}{k_{1j}} + A_j \cdot \exp(\lambda_{1,j} \cdot \delta_j) + B_j \cdot \exp(\lambda_{2,j} \cdot \delta_j) = C_{eq_{j+1}} + \frac{R_{0,j+1}}{k_{1,j+1}} + A_{j+1} + B_{j+1} \quad (40)$$

The third condition implies that for the final layer $B_m = 0$ (since $\lambda_{2,m} > 0$).
The fourth condition gives, since for layer j at $Z_j = \delta_j$:

$$J_j(\delta_j) = -\mu_j \cdot D_j \cdot (A_j \cdot \lambda_{1,j} \cdot \exp(\lambda_{1,j} \cdot \delta_j) + B_j \cdot \lambda_{2,j} \cdot \exp(\lambda_{2,j} \cdot \delta_j) \quad (\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}) \quad (41)$$

and for layer $(j+1)$ at $Z_{j+1} = 0$:

$$J_{j+1}(0) = -\mu_{j+1} \cdot D_{j+1} \cdot (A_{j+1} \cdot \lambda_{1,j+1} + B_{j+1} \cdot \lambda_{2,j+1}) \qquad (\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}) \quad (42)$$

that

$$\mu_j \cdot D_j \cdot (A_j \cdot \lambda_{1,j} \cdot \exp(\lambda_{1,j} \cdot \delta_j) + B_j \cdot \lambda_{2,j} \cdot \exp(\lambda_{2,j} \cdot \delta_j) = \\ = \mu_{j+1} \cdot D_{j+1} \cdot (A_{j+1} \cdot \lambda_{1,j+1} + B_{j+1} \cdot \lambda_{2,j+1}) \qquad (\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}) \quad (43)$$

Now, the profile in each layer j is defined by two parameters A_j and B_j; also there are two (boundary) conditions formulated per layer. So, both parameters A and B can be calculated for each layer. Both equations may be simplified.
With eq.(35),(64), and

$$\gamma_{1,j} = \exp(\lambda_{1,j} \cdot \delta_j) \qquad (-) \quad (44)$$

$$\gamma_{2,j} = \exp(\lambda_{2,j} \cdot \delta_j) \qquad (-) \quad (45)$$

$$p_j = \mu_j \cdot D_j \qquad (\text{m}^2 \cdot \text{s}^{-1}) \quad (46)$$

it follows from the concentration continuity condition that

$$\gamma_{1,j} \cdot A_j + \gamma_{2,j} \cdot B_j - A_{j+1} - B_{j+1} = -E_j + E_{j+1} \quad (\text{mol} \cdot \text{m}^{-3}) \quad (47)$$

with j = 1..(m-1).

The flux continuity condition (condition 4) represented by eq.(43) gives

$$p_j \cdot \lambda_{1,j} \cdot A_j \cdot \gamma_{1,j} + p_j \cdot \lambda_{2,j} \cdot B_j \cdot \gamma_{2,j} - p_{j+1} \cdot \lambda_{1,j+1} \cdot A_{j+1} - p_{j+1} \cdot \lambda_{2,j+1} \cdot B_{j+1} = 0 \quad (48)$$

j = 1..(m-1). For the final layer m, at plane m + 1, the flux J_{m+1} is unknown. Since $B_m = 0.0$, J_{m+1} is to be calculated. (Another option was to assume that $J_{m+1} = 0$ as i done for the zero order reactions. But *and* $J_{m+1} = 0.0$, *and* $B_m = 0.0$ is not a realistic situation because the set of 2m equations would be over-determined. The 2m equations would have 2m + 1 conditions. So, for the first order situation, J_{m+1} #0.0, and can be calculated from the pore water profile equations. J_{m+1} is a loss term in the overall mass budget for the system).

The flux through plane m + 1 reads

$$J_{m+1} = p_m \cdot \lambda_{1,m} \cdot A_m \cdot \gamma_{1,m} \quad (\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}) \quad (49)$$

When just one or two layers are involved, the above conditions can be rewritten to give readable expressions. However, when more layers are involved, this is not longer possible. In Ecowasp, we apply a Gauss elimination procedure to solve the set of (2m-1) linear equations, where m is the number of sediment layers in the system. The m^{th} equation is $B_m = 0.0$, and this is omitted in this Gauss procedure. The unknown variables x{1 .. 2m-1} are the m A and the (m-1) B parameters. In section 3.3.2, this calculation procedure is explained.

In EcoWasp, the layer characteristics, that determine R_0, k_1, C_{eq}, λ_1 and λ_2, are calculated every simulation step. The layer characteristics are part of the fixed layer system (eg. solid content, porosity) or part of the variable layer system (eg. R_0, acceptor situation).

2.4. No reaction

In some cases, ions will show no reactivity, nor adsorption/desorption or precipitation/dissolution, neither production or consumption as a result of microbiological transformations. Chloride is a good example. In such cases, a simple numerical diffusion may be computed, without assuming steady state.

A second possibility is to assume that the pore water concentrations of such components are the same as they are in the overlying water. The error that results from this assumption is minor as long as the sediment-depth is much smaller than the height of the water column.

In EcoWasp, the second possibilities is implemented.

2.5. Mean layer concentrations

For the zero order reaction profiles, it follows for the mean layer concentration C_{mean} in each layer j

$$C_{mean} = [\frac{1}{3}\cdot\alpha_{1,j}\cdot Z_j^3 + \frac{1}{2}\cdot\alpha_{2,j}\cdot Z_j^2 + \alpha_{3,j}\cdot Z_j]_0^{\delta_j}\cdot\delta_j^{-1} \quad (mol\cdot m^{-3}) \quad (50)$$

which can be rewritten as

$$C_{mean} = \frac{1}{3}\cdot\alpha_{1,j}\cdot\delta_j^2 + \frac{1}{2}\cdot\alpha_{2,j}\cdot\delta_j + \alpha_{3,j} \quad (mol\cdot m^{-3}) \quad (51)$$

where δ_j is the thickness of layer j. In case of zero order consumption, $C_{mean} = 0$ for all the layers below the penetration depth.

In case of a first order reaction, C_{mean} follows from

$$C_{mean} = [E_j\cdot Z_j + \frac{A_j}{\lambda_{1,j}}\cdot\exp(\lambda_{1,j}\cdot Z_j) + \frac{B_j}{\lambda_{2,j}}\cdot\exp(\lambda_{2,j}\cdot Z_j)]_0^{\delta_j}\cdot\delta_j^{-1} \quad (mol\cdot m^{-3}) \quad (52)$$

and thus

$$C_{mean} = E_j\cdot\delta_j + \frac{A_j}{\lambda_{1,j}}\cdot\{\exp(\lambda_{1,j}\cdot\delta_j)-1\} + \frac{B_j}{\lambda_{2,j}}\cdot\{\exp(\lambda_{2,j}\cdot\delta_j)-1\}\cdot\delta_j^{-1} \quad (mol\cdot m^{-3}) \quad (53)$$

where E_j is defined according to eq.(35),

2.6. Fluxes

The calculation of the fluxes is very straightforward, following Fick's first law (eq.8). A positive flux is directed downwards.

For all the zero order cases:

$$J_j = -D_j\cdot\mu_j\cdot\alpha_{2,j} \quad (mol\cdot m^{-2}\cdot s^{-1}) \quad (54)$$

where the flux concerns *plane j* between layers j and j-1.

For the first order cases:

$$J_j = -D_j\cdot\mu_j\cdot(\lambda_{1,j}\cdot A_j + \lambda_{2,j}\cdot B_j) \quad (mol\cdot m^{-2}\cdot s^{-1}) \quad (55)$$

Only the J_1-values are needed for further use in the overlying water concentration calculations.

3. ALGORITHMS FOR PORE WATER PROFILE CALCULATIONS

In this section, algorithms are presented for the calculation of pore water profiles and fluxes, and the electron acceptor penetration depth in EcoWasp.

3.1. Penetration depths of electron acceptors

The redox sequence is defined according to Fig.3. This implies that the program has to recognize which ion act as electron acceptor. Here we assume that this has been arranged. In reality, this redox sequence also depends on other variables, such as the pH of the pore water. For an introduction, see e.g. Stumm and Morgan (1970). Due to the layer schematization, the occurrence of micro-environments (e.g. reduced spots within the oxic layers) is also neglected.

To be clear, the fixed and variable layer definition from Fig.4 is repeated here.

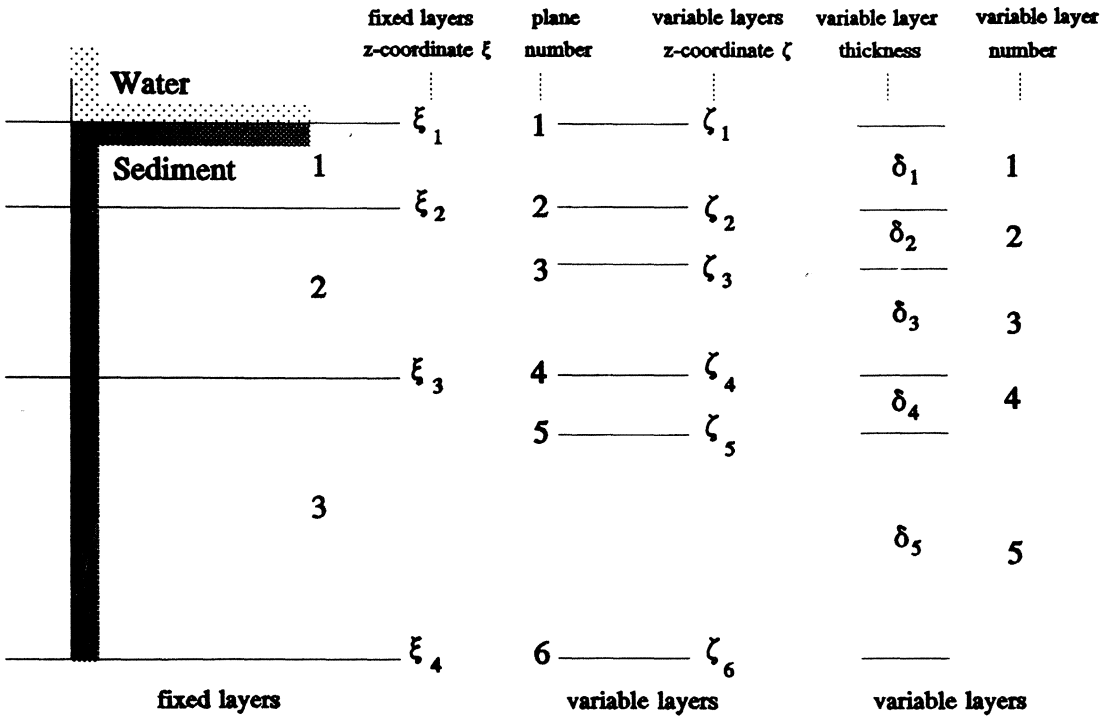


Figure 5. Definition of fixed and variable layers. Note that all ξ-planes are also variable layer planes: ξ_i always coincides with a ζ_j plane, $j \geq i$.

In Table 1 all the equations that are applied are summarized.

The applied scheme is presented in Figure 6 including the criterions and the if-then-else sequences.

The scheme shows how the calculation starts with the penetration depth of the first electron acceptor, which usually is oxygen. First, it is checked whether R_0 is positive or negative. For oxygen, R_0 can be positive in the sediment top layer because of algal production activities. In that case, $\delta_1 = \xi_2$ or $\zeta_2 = \xi_2$ and the penetration depth calculation starts from the second layer. For simplicity, we assume here that $R_0 < 0$. Then the penetration depth is calculated, and it is checked whether the calculated penetration depth δ_1 exceeds ξ_2, the position of the plane between the first two fixed layers (or: the z-coordinate of the second layer). If δ_1 is larger than ξ_2, the first variable layer obviously is similar to the first fixed layer, and, consequently, $\delta_1 = \zeta_2 = \xi_2$. In this case, δ_2, the oxygen penetration into the second sediment layer has to be calculated and $\zeta_3 = \delta_1 + \delta_2 = \xi_2 + \delta_2$ is the total oxygen penetration depth. The depth δ_2 has to be calculated iteratively because $C(\zeta_2)$ is not known. $C(\zeta_2)$ is the estimator in this iteration. In this second fixed layer, R_0-values, porosity and apparent diffusion coefficient general will differ from the values in the first layer. In appendix 1, details on this iteration are given. Once an acceptable δ_2 value is obtained, the check is repeated. When ζ_3 is $> \xi_3$, then $\delta_2 = \xi_3 - \zeta_2$, $\zeta_3 = \xi_3$, and the penetration depth calculation starts again, now including the third fixed layer characteristics. If, on the other hand, $\zeta_3 < \xi_3$, then the penetration depth is known and the second electron acceptor's penetration depth has to be calculated. This starts with an estimate for $C(z = \zeta_3)$, followed by the layer thickness calculation and the solid layer checks.

This procedure is repeated for all acceptors. The last layer is assigned to the remaining layer thickness.

As mentioned in section 3 there are not more than (n_{acc} + n_{fix} -1) variable layers, where n_{acc} is the number of electron acceptors (including the possibility that organic matter itself acts as acceptor), and n_{fix} is the number of fixed sediment layers. Problems arise when a penetration depth exceeds the final plane position ξ_{nfix+1}. This problem is solved by assuming that the layer characteristics for the sediment below that final layer are equal to those of the final layer. The profile of the last acceptor thus extends beyond the final layer, and there is diffusion across the final plane (m+1). This diffusion quantity is subtracted from the flux at the sediment/water interface. This correction is done by routine PenetrationDepthsCorrections (see Table 1, page 51). Consequently, the mass budget is correct; only the processes deep down in the sediment are (slightly) underestimated in this case.

During the calculations the zero order production/consumption routines (Algae, Detritus, Nitrification and ReducedOx, see section 4) are called (by routine CalcZeroOrderProcesses) for each variable layer. After the variable layer computations, all zero order consumption- as well as the zero order production rates are known for all the layers.

The calculations of corresponding fluxes and concentration averages are explained in section 3.4.

Table 1 Summary of equations used for the computation of pore water profile and fluxes

General
There are m layers. Layer 0 is the overlying water. Plane j is between layers (j-1) and j. Plane (m+1) is the lower border of the system. C and R are expressed in units per m^3 pore water volume. The flux J is expressed in units per m^2 system area.

Reaction term R is zero order in C, and positive
The concentration profile of C is described by

$$C_{j,z} = \alpha_{1,j} \cdot (z-\zeta_j)^2 + \alpha_{2,j} \cdot (z-\zeta_j) + \alpha_{3,j} \qquad (\text{mol} \cdot \text{m}^{-3}) \quad (4)$$

with
ζ_j = z-coordinate of plane j between layer (j-1) and layer j.

$\alpha_{2,j}$ for all layers is

$$\alpha_{2,j} = \frac{\sum_{i=j}^{m} R_{0,i} \cdot \delta_i}{D_j \cdot \mu_j} \qquad (\text{mol} \cdot \text{m}^{-4}) \quad (19)$$

$\alpha_{1,j}$, for layers 1.. (m-1) :

$$\alpha_{1,j} = \frac{1}{2 \cdot \delta_j} \cdot \left(\frac{D_{j+1} \cdot \mu_{j+1}}{D_j \cdot \mu_j} \cdot \alpha_{2,j+1} - \alpha_{2,j}\right) \qquad (\text{mol} \cdot \text{m}^{-5}) \quad (20)$$

for j=m :

$$\alpha_{1,m} = -\frac{1}{2 \cdot \delta_m} \cdot \alpha_{2,m} \qquad (\text{mol} \cdot \text{m}^{-5}) \quad (21)$$

$\alpha_{3,j}$, for layer 1 :

$$\alpha_{3,1} = C_0 \qquad (\text{mol} \cdot \text{m}^{-3}) \quad (25)$$

and for layers j=2..m :

$$\alpha_{3,j} = \alpha_{1,j-1} \cdot \delta_{j-1}^2 + \alpha_{2,j-1} \cdot \delta_{j-1} + \alpha_{3,j-1} \qquad (\text{mol} \cdot \text{m}^{-3}) \quad (24)$$

Reaction term R is zero order, and negative.
All the equations above apply. One extra equation for δ_k reads:

$$\delta_k = \sqrt{\frac{-2 \cdot C_{k,0} \cdot D_k \cdot \mu_k}{R_{0,k}}} \qquad (\text{m}) \quad (29)$$

The value $C_{k,0}$ is used as an estimator in the iterative computation needed to solve the set of equations that describes the pore water profile.

Table 1 (Continued)

Reaction term R (also) is first order in C
The concentration profile of C is described by

$$C_{z,j} = E_j + A_j \cdot \exp(\lambda_{1,j} \cdot z) + B_j \cdot \exp(\lambda_{2,j} \cdot z) \qquad (\text{mol} \cdot \text{m}^{-3}) \quad (34)$$

with

$$E_j = \frac{R_{0,j}}{k_{1,j}} + C_{eq,j} \qquad (\text{mol} \cdot \text{m}^{-3}) \quad (35)$$

and

$$\lambda_1 = -\sqrt{\frac{k_{1,j}}{D_j}} \qquad (\text{m}^{-1}) \quad (36)$$

and

$$\lambda_2 = \sqrt{\frac{k_{1,j}}{D_j}} \qquad (\text{m}^{-1}) \quad (37)$$

λ_1 is negative, and λ_2 is positive.
The factors A and B are found after a Gauss-elimination computation.

Fluxes when R is zero order in C
For each layer j, at Z=0, the flux through plane j is

$$J_j = -D_j \cdot \mu_j \cdot \alpha_{2,j} \qquad (\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}) \quad (54)$$

Fluxes when R is first order in C
For each layer j, at Z=0, the flux through plane j is

$$J_j = -D_j \cdot \mu_j \cdot (\lambda_{1,j} \cdot A_j + \lambda_{2,j} \cdot B_j) \qquad (\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}) \quad (55)$$

Mean layer concentrations when R is zero order in C
For each layer j, the mean concentration reads

$$C_{mean} = \frac{1}{3} \cdot \alpha_{1,j} \cdot \delta_j^2 + \frac{1}{2} \cdot \alpha_{2,j} \cdot \delta_j + \alpha_{3,j} \qquad (\text{mol} \cdot \text{m}^{-3}) \quad (51)$$

Mean layer concentrations when R is first order in C
For each layer j, the mean concentration reads

$$C_{mean} = E_j \cdot \delta_j + \frac{A_j}{\lambda_{1,j}} \cdot \{\exp(\lambda_{1,j} \cdot \delta_j) - 1\} + \frac{B_j}{\lambda_{2,j}} \cdot \{\exp(\lambda_{2,j} \cdot \delta_j) - 1\} \cdot \delta_j^{-1} \qquad (\text{mol} \cdot \text{m}^{-3}) \quad (53)$$

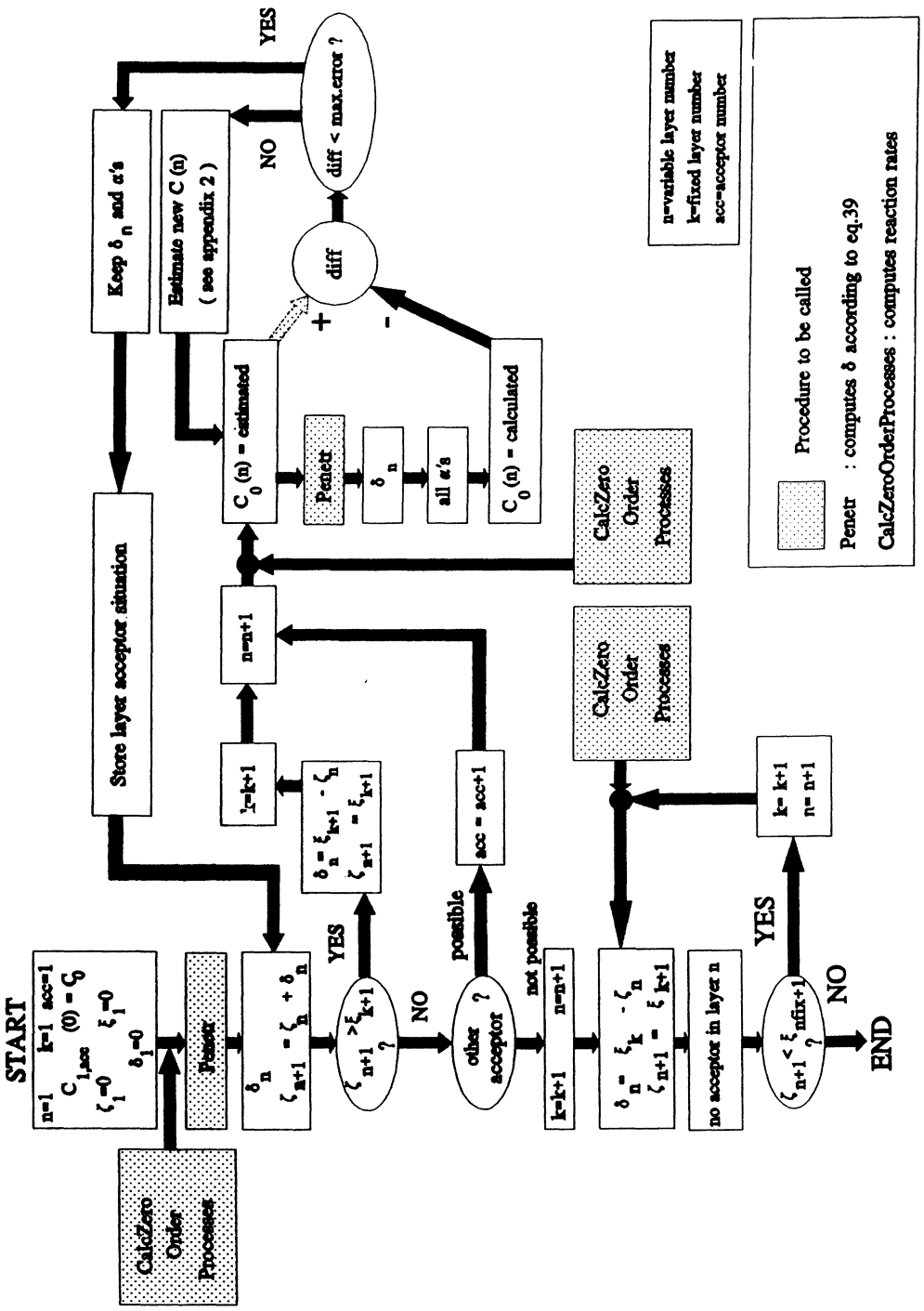
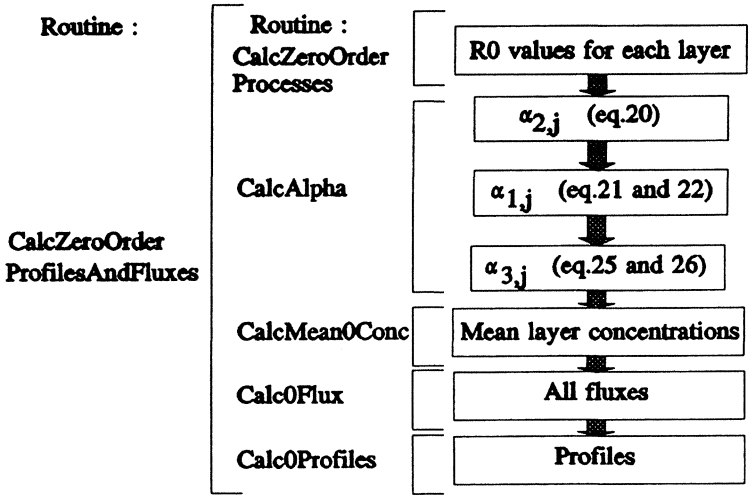


Figure 6. Computation of acceptor penetration depths in EcoWasp, and of the position of the variable layers.

3.2. Pore water profiles of components with a zero order reaction term

3.2.1. Profile calculation for non-electron acceptors



From the procedure described in section 3.1 the several layers j with thickness δ_j, and plane coordinates ζ_j are known, and so are the zero order production and - consumption rates for all the relevant compounds in each of these layers.

The calculation of all α-parameters is performed according to Figure 7. The values of the α-parameters are inserted in the equations described in Table 1. The mean layer concentrations, fluxes and overall profiles are calculated.

Figure 7. Calculation of zero order reaction α-values and layer characteristics.

3.2.2. Profile calculation for electron acceptors

The same procedure as depicted in Figure 7 is applied for electron acceptors. However, only the layers **above** the penetration depth are considered.

3.2.3. Upward penetration of electron donors

In section 3.1 it is described how electron acceptor penetration depths are calculated. Most of the other pore water components determined by zero order processes are produced rather than consumed in the sediment. However, e.g. ammonia oxidizing bacteria (to nitrate, via nitrite) consume ammonia in oxygen containing upper sediment layers. Thus ammonia, that is produced in deeper sediment layers, diffuses upward and is oxidized in the sediment toplayer. Also, sulphide produced by sulphate reduction is reoxidized to sulphate in the sediment toplayers. In addition to the calculation of the penetration depth of electron acceptors, the "penetration height" of these substances should be computed too. However, this would lead to an increasing number of variable layers. Such an implementation is not realized in EcoWasp. Instead, the profiles of these substances are checked on consistency. That is, it is checked whether the pore water concentrations remain positive or not in the considered layers. If not, mean concentrations and fluxes are corrected.

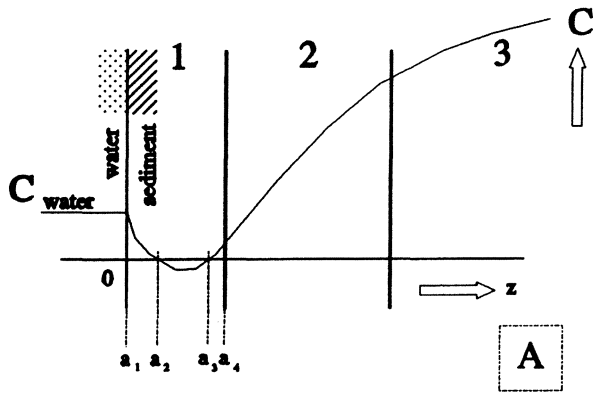


Figure 8. Consumption of upward and downward diffusing component leading to negative concentrations in the sediment top layer. C_{water} is > 0, C diffuses into the sediment.

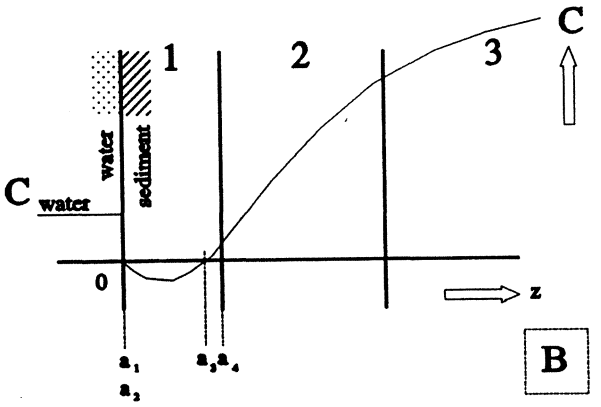


Figure 9. Consumption of upward diffusing component leading to negative concentrations in the sediment toplayer. C_{water} = 0.

Two situations are relevant, shown in Figure 8 and Figure 9; in both cases an interval exists $a_2 < z < a_3$ where $C_z < 0$.

The solutions of the diffusion equations do **not** prevent these possibilities. The concentration -and the flux link conditions are met, resulting in parabolic concentration profiles in each layer.

The check is carried out as follows:

$R_{0,1}$= the reaction rate (zero order) in the sediment toplayer
C_0 = the concentration in the overlying water
C_{a4}= the concentration at position a_4

The penetration depth a_2 of C into the sediment is computed using eq.(29)

$$a_2 = \sqrt{-\left(\frac{2 \cdot C_0 \cdot D_1 \cdot \mu_1}{R_{0,1}}\right)} \tag{56}$$

The upward penetration height (a_4-a_3) is

$$(a_4 - a_3) = \sqrt{-\left(\frac{2 \cdot C_{a_4} \cdot D_1 \cdot \mu_1}{R_{0,1}}\right)}$$

"

$$a_2 < a_3 \tag{58}$$

then $C_z = 0$ on the interval $a_2 < z < a_3$. The average concentration in layer 1 has to be corrected and equals

$$\overline{C_1} = \frac{1}{a_4} \cdot \left[\int_0^{a_2} C_z \cdot dz + \int_{a_3}^{a_4} C_z \cdot dz\right] \tag{59}$$

The fluxes need no correction.

In the situation of Figure 9, the concentration correction is identical to that of situation Figure 8. Now $a_2 = 0$, since $C_0 = 0$. The calculated flux J_1 through plane 1 (the sediment/water interface) is >0, since $\alpha_{2,1} \# 0$ for this component (see also section 2.5). So, J_1 has to be changed to $J_1 = 0$.

The corrections mentioned in this section are performed by routine CheckZeroConsistency which in turn is called by CalcZeroOrderProfilesAndFluxes. The check is only relevant for those components i with a zero order reaction term $R_{0,i,j} < 0$.

3.3. Calculation of pore water profiles for components with a first order reaction term

In the set of equations (35),(64),(44)-(46), the terms E_j, $\gamma_{1,j}$ and $\gamma_{2,j}$, and p_j are introduced. The linear set of equations is solved with a Gauss elimination procedure.

For each layer j (j = 1..m, m = number of variable layers) there are two unknowns A_j and B_j, except for the last layer where $B_m = 0$ (section 2.3). Consequently, there are (2m-1) unknowns. For the m layers there are (m-1) concentration continuity conditions; there is one extra condition for plane 1 (eq.(38)). There are (m-1) flux continuity conditions for the planes 2..m between layers 1..m (eq.(47)).

The unknown variables now are $\mathbf{x} = \{x_1..x_{2m-1}\}$, where $x_j = A_j$ (j = 1..m), and $x_{m+j} = B_j$ (j = 1..m-1).

The (2m-1) equations read

$$\sum_{j=1}^{2m-1} \beta_{i,j} \cdot x_j = S_i \qquad (60)$$

where the vector $\mathbf{x} = \{x_1..x_{2m-1}\}^T$ has to be found.

The coefficients and the right hand terms S need to be assessed. The first m equations concern the concentration continuity conditions (plane 1 included).

It follows that

$\beta_{i,i-1} = \gamma_{1,i-1}$,i= 2 .. (m)

$\beta_{i,m+i-1} = \gamma_{2,i-1}$,i= 2 .. (m)

$\beta_{i,i} = -1$,i= 1 .. (m)

$\beta_{i,m+i} = -1$,i= 1 .. (m)

For i = 1 (the first layer) only the last two equations are relevant.

The right hand terms are

$S_i = -E_{i-1} + E_i$,i= 2 .. (m)

$S_1 = -C_0 + E_1$

The (m-1) diffusion continuity conditions for the rows (m + 1) to (2m-1) give:

$\beta_{i+m,i} = p_i \cdot \lambda_{1,i} \cdot \gamma_{1,i}$,i= 1 .. m

$\beta_{i+m,i+m} = p_i \cdot \lambda_{2,i} \cdot \gamma_{2,i}$,i= 1 .. m

$\beta_{i+m,i+1} = -p_{i+1} \cdot \lambda_{1,i+1}$,i= 1 .. (m-1)

$\beta_{i+m,i+m+1} = -p_{i+1} \cdot \lambda_{2,i+1}$,i= 1 .. (m-1)

The right hand terms are

$S_i = 0$,i= (m+1) .. (2m-1)

By this, all the equations are known. Note, that there is no flux continuity equation for the first plane, since this is not part of a boundary condition; it is a model outcome and it affects the composition of the water phase.

The above set of equations is solved using a Gauss elimination procedure. Pivoting is performed: the row containing the largest coefficient is subtracted from the ones containing the smaller coefficients. Starting with $\beta_{i,1}$, the largest of all i $\beta_{i,1}$ values (say, row k) is kept; all the other rows i are scaled to this largest $\beta_{k,1}$ value. The row k $\beta_{k,j}$ values are subtracted from the other $\beta_{i,j}$ values (i#k). So, only the row k β-values are stored in a new matrix, at row 1. Then the procedure is repeated for the $\beta_{i,2}$ coefficients, the first row k left out of this procedure. Finally the upper triangle of a (2m-1)*(2m-1) matrix, named **M**, is

filled with newly calculated values β'_{ij}; the lower triangle is empty. The determinant Det (M) of this matrix

$$Det(M) = \prod_{i=1}^{2m-1} \beta'_{i,i} \qquad (61)$$

is needed to check the consistency of the matrix; it has to be #0, otherwise there is no solution for this set of equations.

3.4. Mean fixed layer concentrations

The mean concentrations for the fixed layers follow directly from the mean pore water concentrations for the variable layers (Figure 5):

$$C(sol)_{l,mean} = \frac{1}{\xi_l} \cdot \sum_{j=first}^{j=last} \delta_j \cdot C_{j,mean} \qquad (62)$$

where 'first' is the number of the first variable layer being part of the fixed layer, and 'last' the last variable layer.

3.5. Necessary corrections

3.5.1. Mass budget corrections

Steady state is assumed in EcoWasp from time step to time step. The change from one profile to the next, however, comes with a mass budget problem. This is accounted for by assigning the difference to one of the layers; in EcoWasp, the overlying water is chosen for this correction. Although the effect of this correction has not been fully tested, we expect that it will be minor in most cases because the pore water volume usually is much smaller than the volume of the overlying water. Moreover it concerns concentration *differences* in the pore water (from the profile in one time step to the one in the next time step).

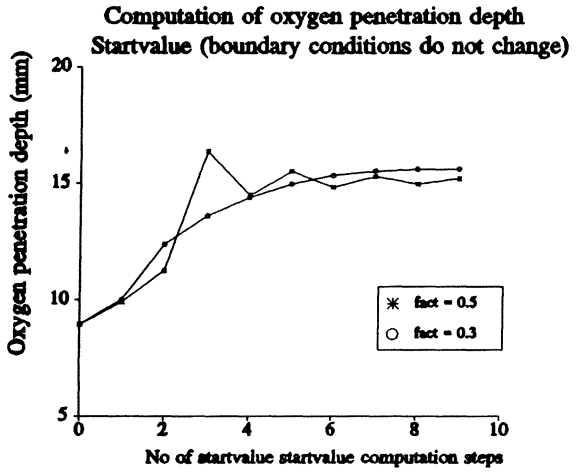


Figure 10. Computation of oxygen penetration depth. Start value computation. Fact determines the contribution of the new value in the final value.

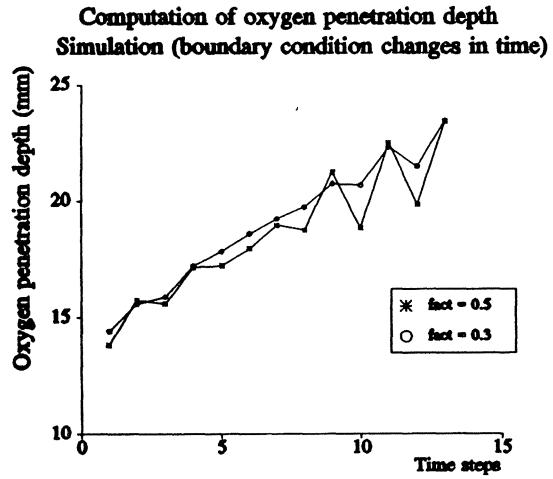


Figure 11. Computation of oxygen penetration for some simulation steps. Fact determines the contribution of the new value in the final computed value.

3.5.2. Non-steady state corrections

The profiles are computed using state variable data from the previous time step. Repeating the computation, using the new concentration values, would result in a different profile. Thus, subsequent computations (from time step to time step) may show alterations around the 'real' profile. This is corrected for by assuming that the mean layer concentrations (that have to be used for the computation of all the reaction rates) are not those as computed from the pore water profiles, but have some value between the previous value and the computed value. This means that a more smooth change in reaction rates is

achieved (Figure 10 and Figure 11 for oxygen, Figure 12 and Figure 13 for nitrate).

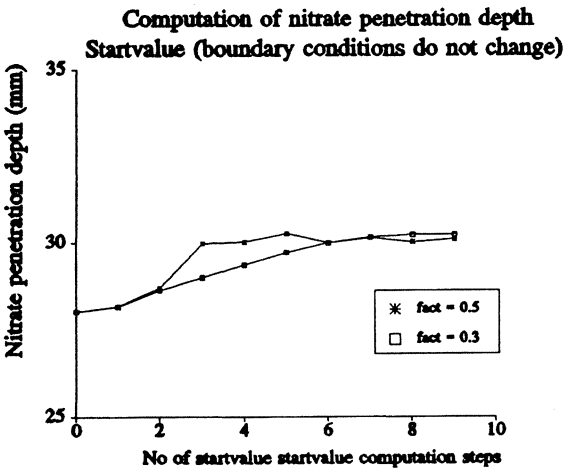


Figure 12. Computation of nitrate penetration depth. Start value computation. Fact determines the contribution of the new value in the final value.

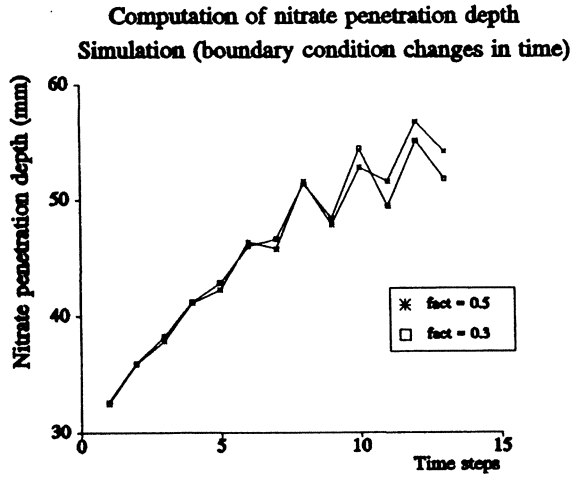


Figure 13. Computation of nitrate penetration for some simulation steps. Fact determines the contribution of the new value in the final computed value.

The above mentioned relaxation method does not prevent all oscillations and other instabilities. It may be discussed whether such alterations are important regarding all kinds of other uncertainties, but numerically it is a rather unpleasant behaviour. Therefore, we implemented a second adaptation: each profile computation is done more than once per time step using the mean pore water concentrations from the previous iteration. In Figure 14 and Figure 15 it is illustrated how the oxygen and the nitrate penetration depths iteratively reach

their final value. In Figure 16, the results for four subsequent simulation steps for oxygen and for nitrate are shown. Regarding computation time, three iterations seems to be satisfactory. In Figure 17 and Figure 18 the result of a test simulation using three iteration steps per time step is illustrated. Results from the first test (no extra iteration, a relaxation factor 'fact' only) are included for comparison.

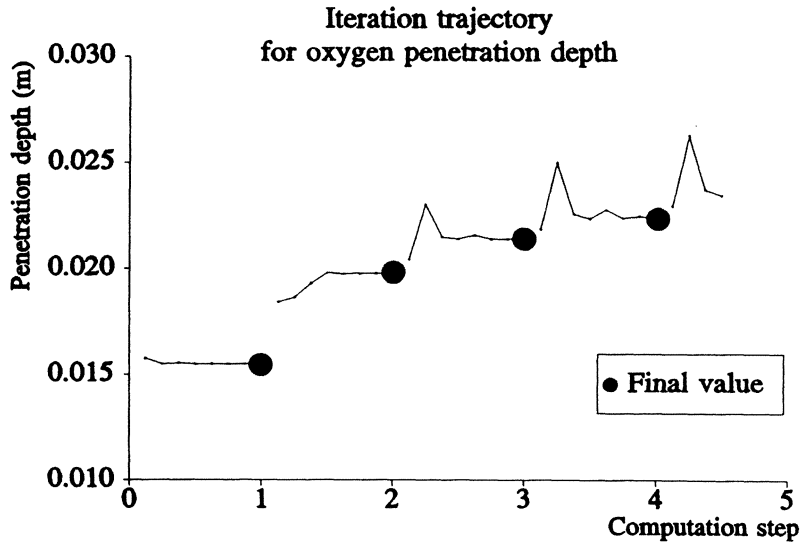


Figure 14. Iteraion trajectory for oxyge penetration depth. Each time step, the conditions in the water and in the sediment have changed. During an iteration, the conditions do not change.

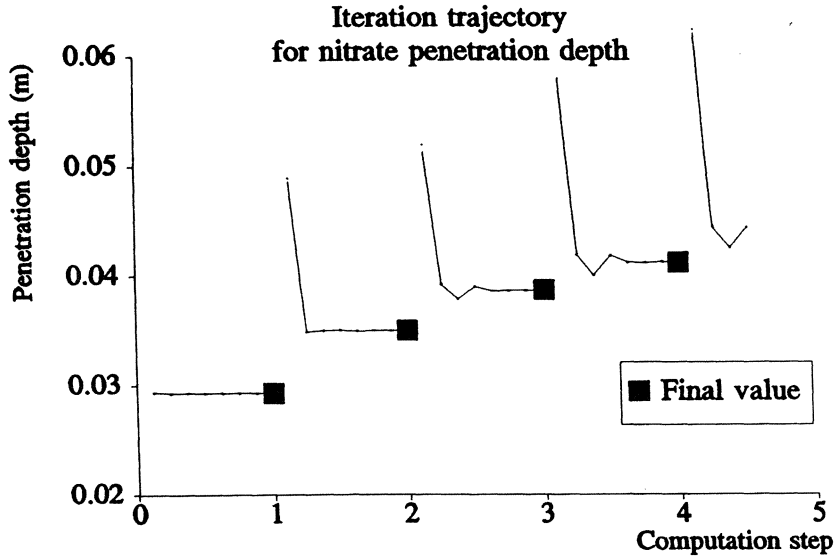


Figure 15. Iteration trajectory for nitrate penetration depth. Each time step the conditions in the sediment and in the water have changed. During the iteration, the conditions are unchanged.

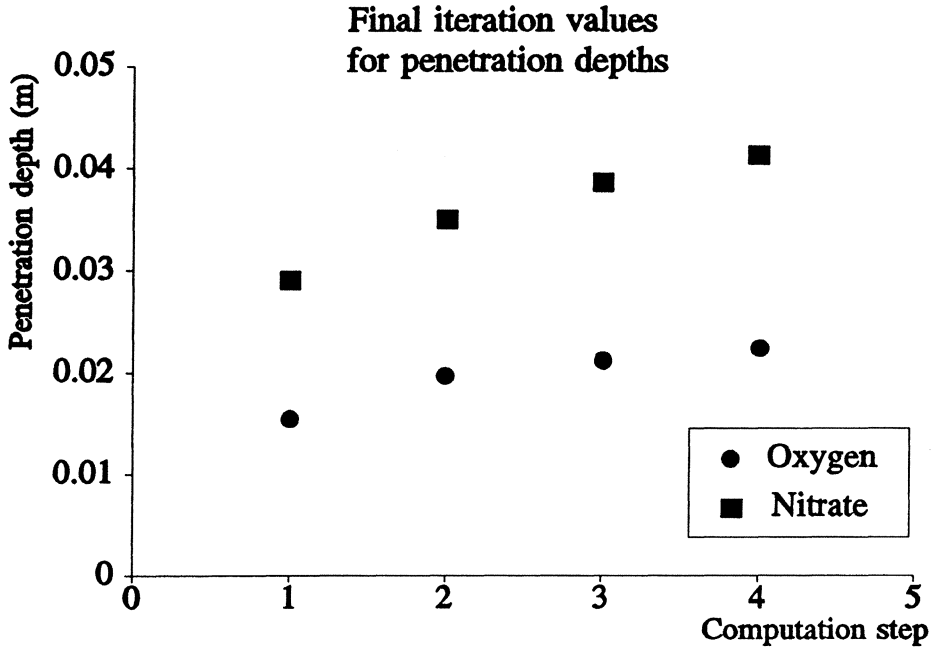


Figure 16. Penetration depths for oxygen and nitrate using multiple iterations. Results from Figs. 14 and 15.

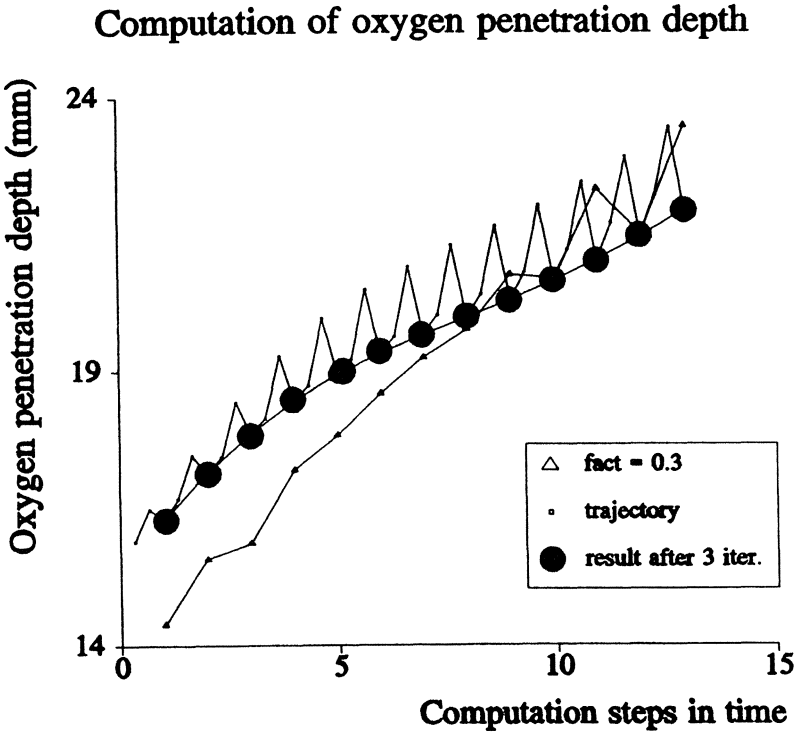


Figure 17. Oxygen penetration depth computation including trajectory and start values. Results from computations without iterations are also shown (fact = 0.3).

It can be seen in Figure 17 and Figure 18 that the iteratively computed penetration depths differ from the ones that result from the relaxation method. The alterations that disturb the relaxation results have disappeared when the iterative method is applied.

In future, this computation method may have to be improved.

3.5.3. Penetration depth corrections

When an electron acceptor penetration depth exceeds the final (m + 1) plane position, the calculated fluxes need to be corrected. The flux J_{m+1} through the final plane is subtracted from the value J_1, the flux from the overlying water into the sediment. So, the effect of the sediment on the overlying waters changes. The exchange **between** the sediment layers is **not** changed, only the processes deep down in the sediment are underestimated.

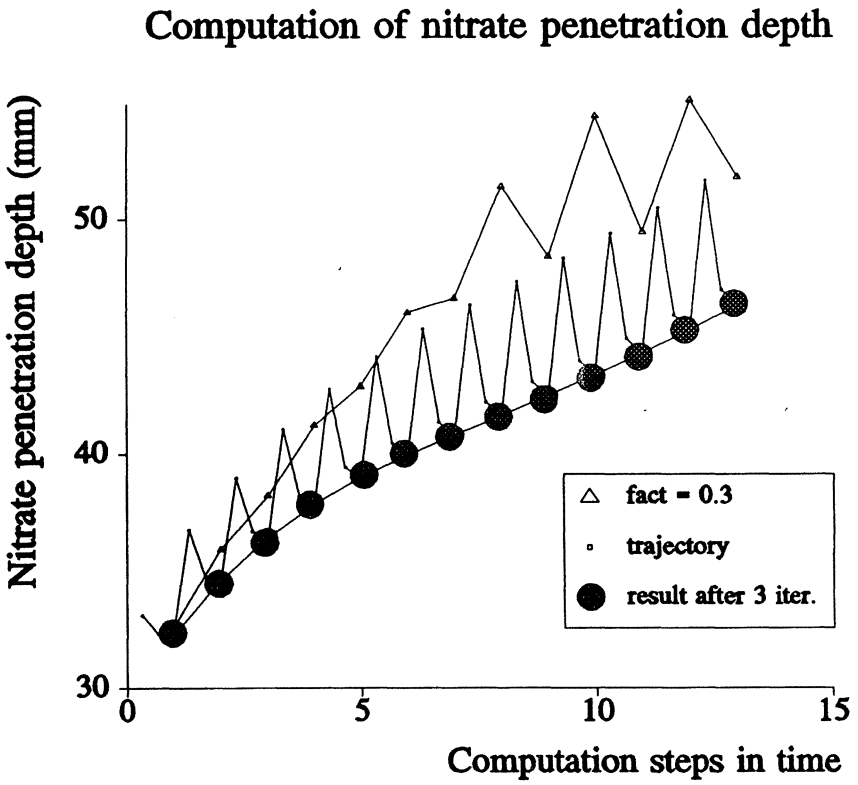


Figure 18. Nitrate penetration depth computation including trajectory and start values. Results from computations without iterations are also shown (fact = 0.3).

4. ASSESSMENT OF THE ZERO ORDER REACTION TERM R_0 AND THE FIRST ORDER REACTION TERM R_1.

4.1. Reactions involved

The reaction term R in eq.(1) represents the effect of biochemical transformations and other chemical reactions. The formulation of R determines the solution of the diffusion-reaction equation. First-order and zero-order equations are solvable, but other reaction orders will cause serious mathematical problems. Therefore, the chemical and biological -or biochemical- reactions are approximated as first-order or as zero-order reactions in EcoWasp. Most biological reactions, however, follow a so called Monod-shaped dependency of the reacting component: the reaction order smoothly changes from zero to one. Here, this behaviour is idealized into a pseudo zero-order description. Also, many chemical reactions have exotic reaction orders, but they all are described as pseudo-first or pseudo-zero order reactions in EcoWasp. The reaction rate constant then is the product of the real reaction rate constant and a function that contains the deviations from the assumed linearity or the first order characteristic. The zero- and first-order approximations are outlined in section 4.2. In section 4.3, chemical and biological reactions involved are summarized.

Biochemical transformations may concern bacterial mineralization processes, bacterial transformations of inorganic material, algal production processes and results of other biological activities.

Chemical reactions mainly consist of adsorption reactions such as phosphorus binding to iron- or aluminum containing solids: the anions adsorb onto the positively charged solid materials. Other important adsorptions concern the cation-humics interactions. Also precipitation/dissolution reactions may be important.

The reaction terms R_0 (zero order) and R_1 (first order) have to be quantified each time pore water profiles and fluxes have to calculated needed, and, they have to be quantified for each relevant layer. Therefore the mineralization and the adsorption/desorption characteristics have to be quantified.

The solids distribution is important for the assessment of adsorption characteristics, porosities and the organic carbon content, among others.

4.2. The reaction order

The diffusion equation can be solved analytically when the reaction term (R) contains zero (R_0) and/or first order (R_1) terms only.

In almost all the cases where biochemical processes are involved, we assume that the reaction is zero order in C.

However, in some cases, depletion of one of the reaction components occurs and the zero order assumption would result in negative concentrations. Usu-

ally, a Monod-type term is introduced into the reaction term R to avoid this problem:

$$R_0 = R_0' \cdot \frac{C}{K_C + C} \qquad (\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}) \quad (63)$$

where K_C (mol.m^{-3}) is a Monod-constant and R_0' (mol.m^{-3}.s^{-1}) is the maximum reaction rate. For large values of C, R = R' and R is zero order in C. But, when C < K_C, R = R'.C/K_C and R is first order in C. This continuous change from zero to first order makes it impossible to solve the diffusion equation analytically. In EcoWasp, we use concentrations C, resulting from the *previous* time-step calculations. This is explained and refined in section 3.5.2. Obviously, this is not completely exact, but the error probably remains minor, particular for small time steps. In this way, the equation stays zero order in C for all cases.

Most chemical reactions are considered first order in EcoWasp. Here, also a problem arises since e.g. precipitation reactions usually are *not* first order in C, but may have quite exotic orders. To avoid this, the non-first order reactions are linearized or even made zero-order using the conditions at the end of the previous timestep. The linearization or the transformation into a zero order description is performed using relations and parameters that describe the real reaction. By doing this, other problems are avoided also. In this way, all processes become uncoupled from time step to time step, even when more then one component is involved in any reaction.

4.3. Reactions

4.3.1. Adsorption reactions

When a component adsorbs onto a solid, the relationship between the equilibrium concentration of the dissolved component in the (pore) water C_{eq} (mol.m^{-3} pore water) and its adsorption concentration C_{ads} (mol adsorbed.m^{-3} system volume) is given by an adsorption isotherm. The description of an adsorption isotherm as used in EcoWasp is reported elsewhere (Brinkman, 1979; Brinkman, 1993-a). Here, a general outline will be given. We assume that the adsorption rate is insufficient to obtain an equilibrium situation every time step.

Consequently, the adsorption rate has to be accounted for. The reaction term R_1 usually is described as

$$R_1 = -k_1 \cdot (C - C_{eq}) \qquad (\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}) \quad (64)$$

where k_1 is an adsorption rate constant (s^{-1}). In this equation, that is first order in C, C_{eq} is a function of C_{ads} following a Langmuir adsorption isotherm:

$$C_{ads} = \frac{K_{ads} \cdot C_{eq} \cdot Ads_{max}}{1 + K_{ads} \cdot C_{eq}} \cdot [solid] \qquad (\text{mol} \cdot \text{m}^{-3}) \quad (65)$$

Ads_{max} = adsorption maximum onto solid (mol.g(solid)$^{-1}$)

[solid] = solid content (g(solid).m^{-3})

C_{ads} = present adsorption (mol.m^{-3})

K_{ads} = adsorption equilibrium constant (m^{-3}.mol^{-1})

C_{eq} = adsorption equilibrium concentration in the liquid phase (mol.m^{-3})

In EcoWasp, a more complicated Langmuir adsorption isotherm is used (Brinkman, 1979; Brinkman & Van Raaphorst, 1986; Brinkman, 1993-a).

The value of C_{eq} from eq.(65) is calculated by calling routine **Adsorption**. In this routine, all the adsorptions of a component onto all the possible adsorbents are taken into account. This implies that a distribution of each component over the several adsorbents is computed.

The rate constant k_1 from eq.(64) is calculated by calling routine **CalcAdsorptionRate**. Adsorptions onto different adsorbents are taken into account. The solids contents also determine the rate constant, mainly because the active surface (m^{-2} surface.m^{-3} pore water) increases with increasing adsorbent content:

$$k_1 = \frac{1}{\mu} \cdot \sum_{i=1}^{nsolid} k_{1_i}{}' \cdot [solid_i] \qquad (66)$$

where [solid$_i$] is the solid concentration (g.m^{-3}(system volume)), μ the porosity (-) and k'$_{1,i}$ the first order reaction rate constant (mol.m^{-3}.s^{-1}.(g(solid).m^{-3}(system volume)$^{-1}$).

This approximation implies that after the solution of the diffusion equation, the new adsorption value C_{ads} has to be calculated for each relevant adsorbent:

$$C_{ads,t=t2} = C_{ads,t=t1} + \int_{t=t1}^{t=t2} R_1 \cdot dt \qquad \text{(mol • m}^{-3}\text{ system volume)} \quad (67)$$

This C_{ads}-value is used for the calculation of C_{eq} in the subsequent timestep of the simulation. Thus, the values used for C_{eq} and C_{ads} always follow from the previous timestep.

4.3.2. Primary production

Light penetrates in the sediment toplayer and primary production (mainly by diatoms) occurs. The accompanying nutrient uptake and oxygen production rates are calculated by the procedure **Algae**. The light availability results from a separate procedure, the nutrient availability follows from the concentrations at the end of the previous calculation step. As a consequence, the algal production and consumption terms that appear in the diffusion equation are

pseudo zero-order in the relevant components and thus contribute only to R_0-terms in the diffusion equation.

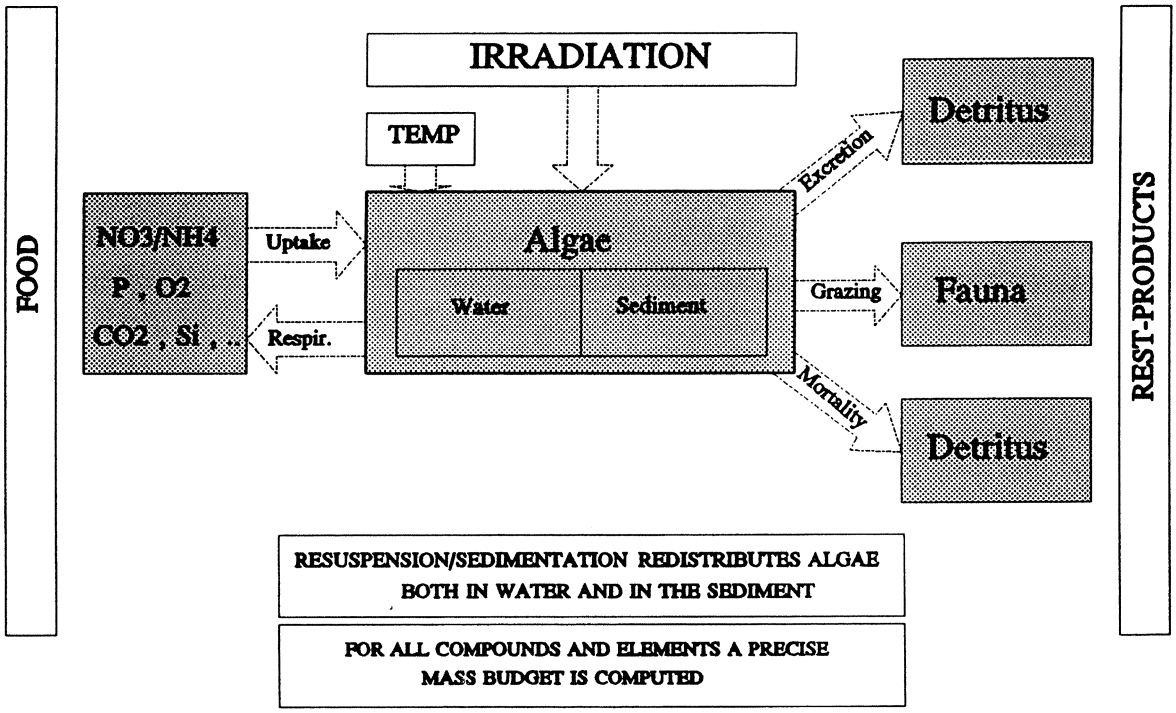


Figure 19. Schematic representation of primary production processes implemented in EcoWasp.

Algae (Figure 19) is called once per layer during the establishment of the variable layers because it not only computes the primary production and thus the oxygen production rate (which will only be relevant in the uppermost sediment layer) but it also provides the respiration and mortality rates of the algae. Algae can be present in all sediment layers as a result of e.g. bioturbation. Thus, **Algae** has effect on the consumption and production rate of all kinds of ions in all layers.

4.3.3. Fauna dynamics

Animals living in the sediment partly feed upon planktonic components as algae or detritus. Other species feed upon sedimentary matter. Respiration and animal growth cause a change of mineral concentration. These changes, or actually, the rate of these changes, act on restricted layers. In EcoWasp, the layer that contains the food, and the layer that receives the respiratory products have to be defined. Thus, these processes (Figure 20) contribute to the zero order R_0-terms in the diffusion equations.

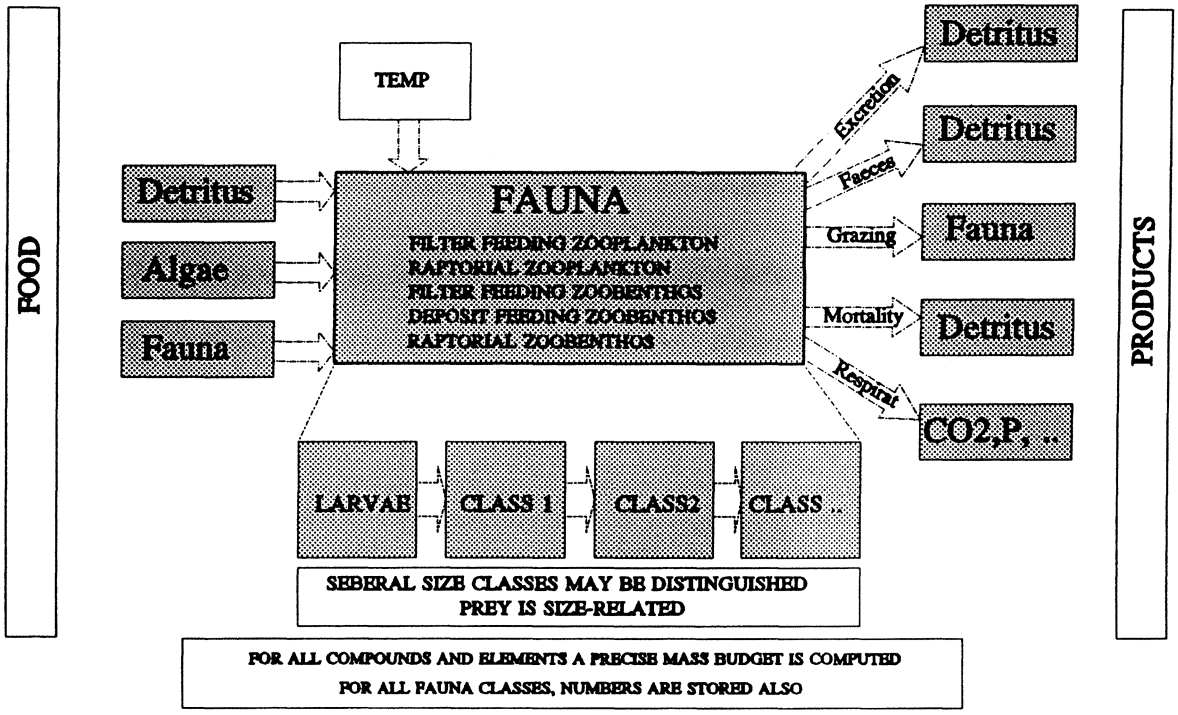


Figure 20. Schematic presentation of fauna dynamics description.

All the fauna activities are computed by the routine **FaunaDynamics** which computes changes per *fixed* sediment layer only, and *not* per variable layer. The reason for this is that, according to the EcoWasp definition, all fauna species live, feed and respire at very distinct depths. These depths may coincide with a very thin variable layer, which would inevitably lead to serious numerical problems. Because of this, **FaunaDynamics** is called before the pore water profile calculations starts, and *not* during the establishment of the variable layers. The resulting rates are assigned to the fixed layers, and according to the relative layer thicknesses they are redistributed over the relevant variable layers.

4.3.4. Mineralization and electron acceptors

Detrital material with the general stoichiometric composition $C_cH_hO_oP_pN_n$ is transformed by bacteria into the components CO_2, H_2O, H_2PO_4_ and NH_4+.

Among others, the sedimentary content of organic, degradable material and the availability of electron acceptors determine the rate of the transformation, and so the rate at which the electron acceptor is consumed, and at which the products are produced. All these rates appear as zero order terms in EcoWasp. In procedure **Detritus** (Figure 21) the mineralization rates, and the production and the consumption rates of all relevant inorganic and organic components,

are calculated. The products ammonium and reduced components (a rest part consisting of sulphides, methane, and other products) may be oxidized in the sediment toplayer(s) where oxygen is present (see sections 4.3.5 and 4.3.6). In each compartment, **Detritus** has to be called once per variable layer during the establishment of these variable layers.

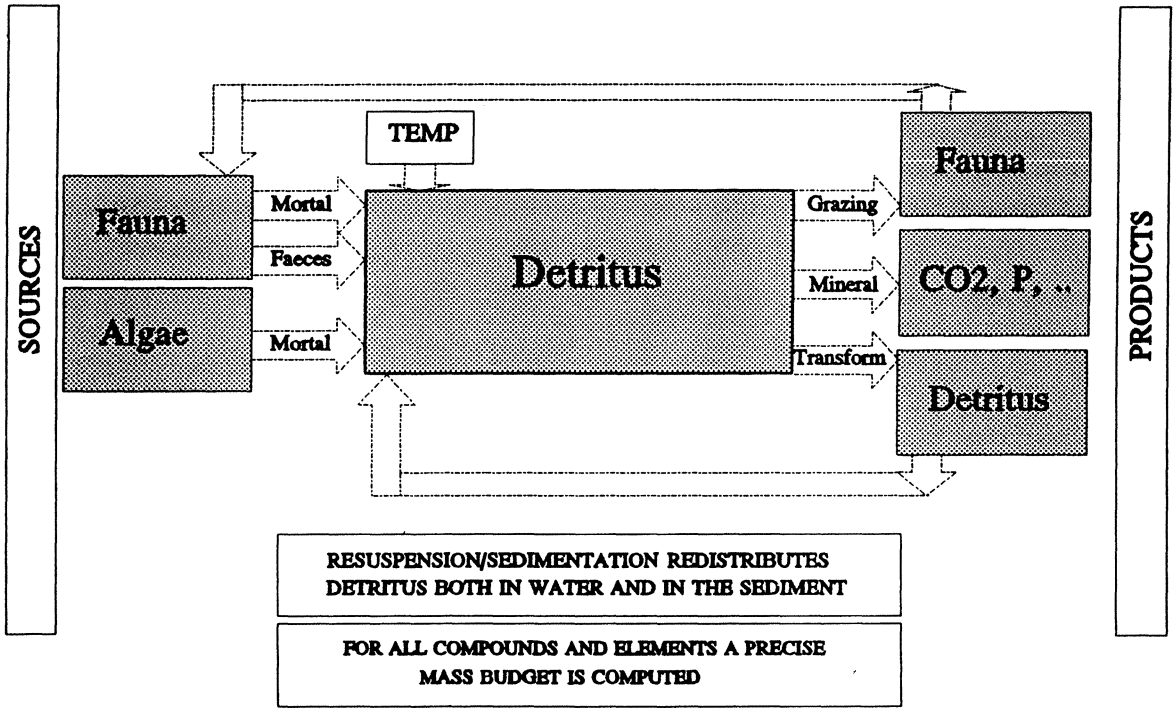


Figure 21. Schematic representation of detritus processes as implemented in EcoWasp.

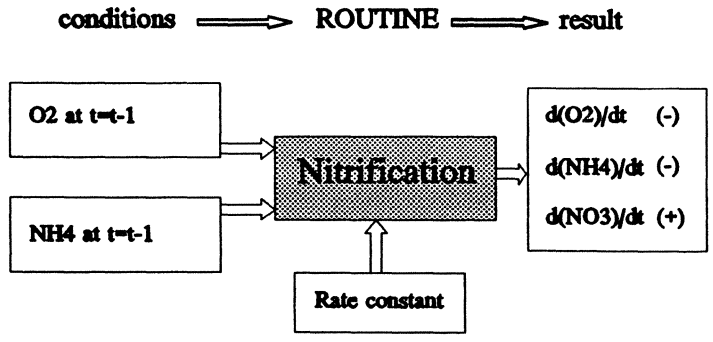


Figure 22. Schematization of nitrification computation in EcoWasp.

4.3.5. Nitrification

In the sediment toplayer(s) where oxygen and ammonium are present, biochemical ammonium oxidation to nitrate takes place. Ammonium is formed in each layer as a product of the mineralization process and diffuses upward. Procedure **Nitrification** calculates the oxidation rate and the associated oxygen and ammonium consumption and nitrate production (Figure 22). These data are needed for the calculation of the oxygen penetration depth and the ammonium and nitrate profiles (and, of course, fluxes). For each compartment, **Nitrification** needs to be called for each oxygen containing layer including the overlying water.

Nitrification assumes a pseudo-zero order reaction with oxygen and ammonia as reacting substances. Temperature also is an important parameter.

4.3.6. Oxidation of other reduced components

In deeper sediment layers where no oxygen or nitrate is present to serve as electron acceptor, sulphide, methane and other reduced products are produced. These products diffuse from these deeper sediment layers upward to the surface where they may be oxidized in those sediment toplayer(s) where oxygen is present. In EcoWasp, this production of reduced substances and the subsequent oxidation in the sediment toplayer(s) is lumped. We assume that only one 'specific' reduced compound is produced as a breakdown product of organic matter. The production rate of this organic reduced compound is computed in procedure **Detrtius**. **ReducedOx** (Fig.20) calculates the oxidation rate of this reduced component and so the consumption rates of oxygen and the production rate of carbon dioxide, which is the only product of this oxidation. **ReducedOx** is called once per calculation step, and only for those layers that contain oxygen.

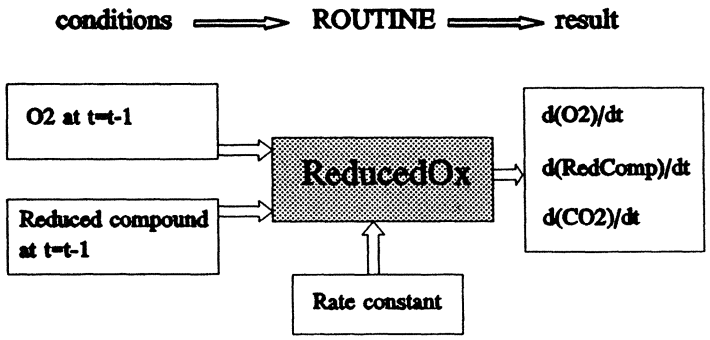


Figure 23. Schematization of oxidation of reduced compounds that lumps sulphides, methane and other products.

4.4. The oxidation state in the variable layers

For a number of sediment calculations the oxidation state is important.

The adsorption properties of the sediment partly depend on the presence of iron(III)oxides which is restricted to the layers where O_2 and NO_3_are present. It must be mentioned that in sediments also iron(III) and manganese(IV) may act as electron acceptors. When the oxygen- plus nitrate penetration depth decreases, iron(III) will be reduced first, before sulphate reduction begins. Iron(III) is present in the sediment already as solid Fe(III)-oxides. After reduction, Fe (II) may be oxidized when oxygen becomes again available. Upward transport of Fe(II), or downward transport of Fe(III) will influence this process. For manganese, that is reduced from Mn(IV) to Mn(II) before nitrate reduction occurs, the process is similar. Thus, these components act as a buffer in the system, thus putting a brake on the rate at which the anaerobic border moves upward or downward. We did not implement the result of the iron- and/or manganese reduction/oxidation process, but assumed that on the longer term, the net effect is be close to zero. With no doubt, this means that the computation of the thickness of the oxidized zone in the sediment, that coincides with the Fe(III)/Fe(II) border, overestimates the real changes.

4.5. Summary

Oxygen diffuses from the overlying water into the sediment, and/or can be produced in the upper sediment layer by benthic algae. The oxygen consumption rate and the diffusion rate together determine the penetration depth of oxygen into the sediment.

In the oxygen containing sediment toplayer, ammonium is oxidized to nitrate. Together with diffusion and the nitrate consumption rate in the sediment layers where nitrate acts as the electron acceptor, the nitrate penetration depth is determined. The penetration depths of oxygen and nitrate together determine the profiles of all other compounds to a great extent.

For bookkeeping and minimizing of numerical errors, a number of fixed sediment layers are distinguished. The fixed layers, together with the variable layers determined by the acceptor penetration depths determine the overall layer structure of the sediment during the computation of profiles and fluxes. When e.g. the 'oxygen'-layer penetrates into the second fixed layer, there are two oxygen-sublayers with different organic material content and different mineralization rates.

The procedure providing the zero order mineralization rates has to be called (only) each time when a new sublayer is subject of the computation. Since there are (nfix + nacc -1) variable layers, so (nfix + nacc-1) times the zero order process procedures have to be called for each computation time step.

5. SUMMARY OF PORE WATER CALCULATION ROUTINES

The processes described in the previous sections are compiled into a number of computer program procedures calculating pore water profiles and dissolved component fluxes. Together, these procedures present the framework of the pore water profiles calculation.

These procedures are listed in Table 2.

Table 2 List of pore water profile calculation procedures

nr	Subject of calculation	Name	Level*
I Routines called in advance, once per fixed sediment layer			
1	Zoobenthos processes in sediment	FaunaDynamics	0
II Pore water profile computation routines			
2	Main procedure calling all subroutines	CalcPoreWaterProfilesAndFluxes	1
3	Profiles and fluxes of components that have zero order process characteristics (mineralization, chemolithotrophic transformations)	CalcZeroOrderProfilesandFluxes	2
4	Penetrationdepth and variable layers thickness	CalcVariableLayers	3
5	Primary production in sediment toplayer	Algae	4
6	Mineralization in all layers	Detritus	4
7	Ammonium oxidation	Nitrification	4
8	Oxidation of all other reduced compounds	ReducedOx	4
9	Computation of mean concentrations, fluxes and profiles	CalcMean0Conc, Calc0Flux, Calc0Profiles	3
10	Profiles and fluxes of components that have first order process characteristics (adsorption/desorption and precipitation/dissolution)	CalcFirstOrderProfilesandFluxes	2
11	Adsorption equilibrium	Adsorption	3
12	Adsorption rates	CalcAdsorptionRates	3
13	Computation of mean concentrations, fluxes and profiles	CalcMean1Conc, Calc1Flux, Calc1Profiles	3
14	Profiles and fluxes of components that do not react	CalcNoReactionProfilesAndFluxes	2
15	Corrections dealing with the sudden profile change from timestep to timestep	TimeStepCorrections	2
16	Corrections dealing with a possible penetration of electron acceptors beyond the system lower border	PenetrationDepthCorrections	2
17	Recomputing variable layer concentrations and fluxes to fixed sediment layer concentrations and fluxes	VariableLayersToFixedLayers	2

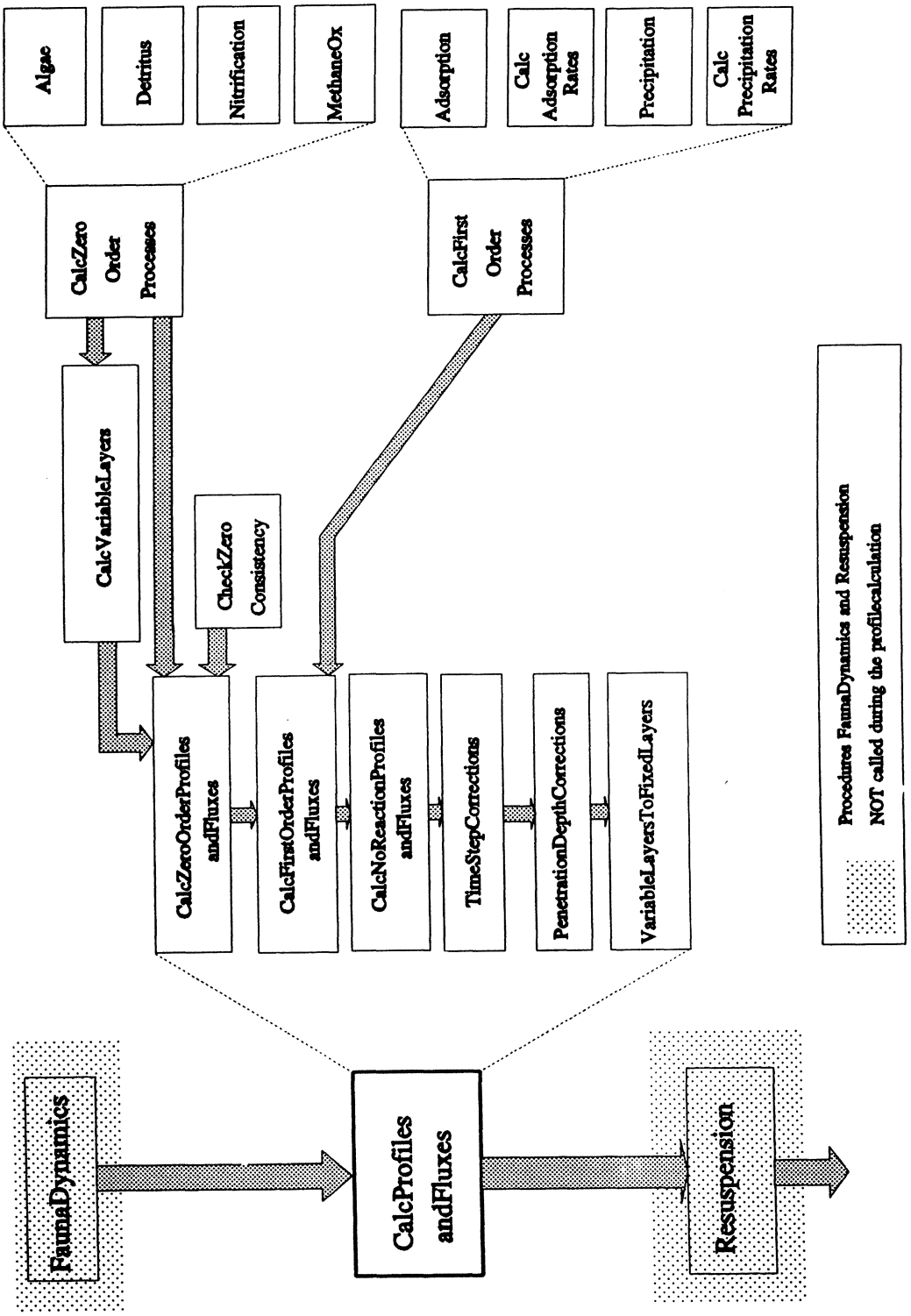


Figure 24. Calculation of pore water profiles: routine calling scheme.

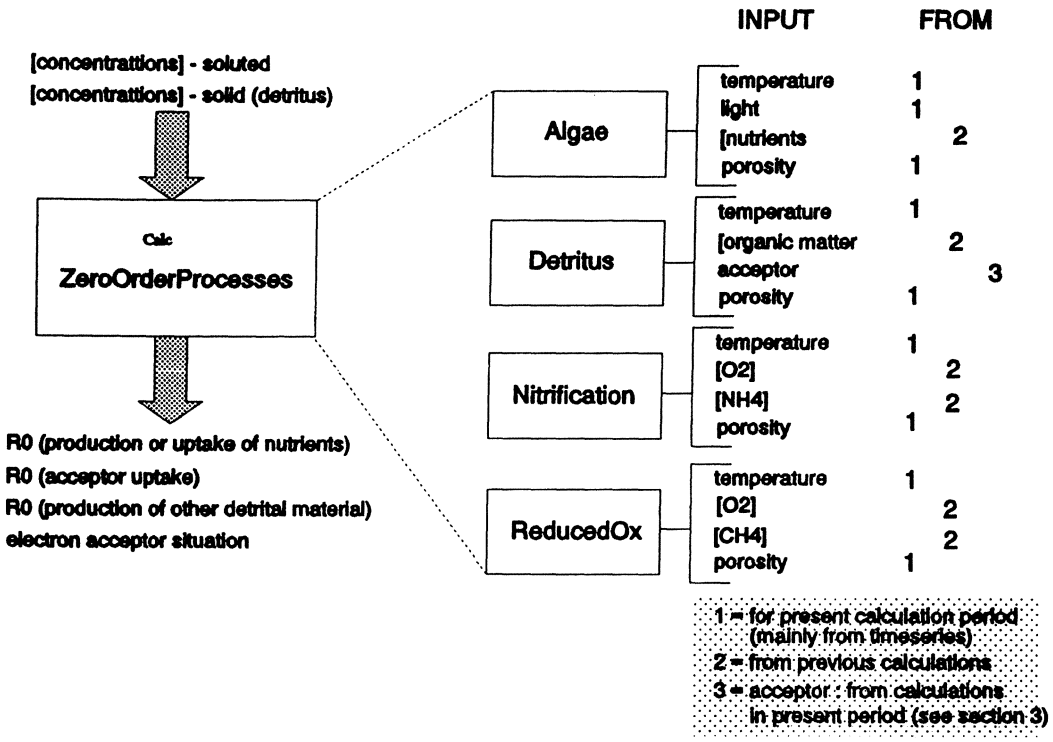


Figure 25. Computation scheme for zero order processes.

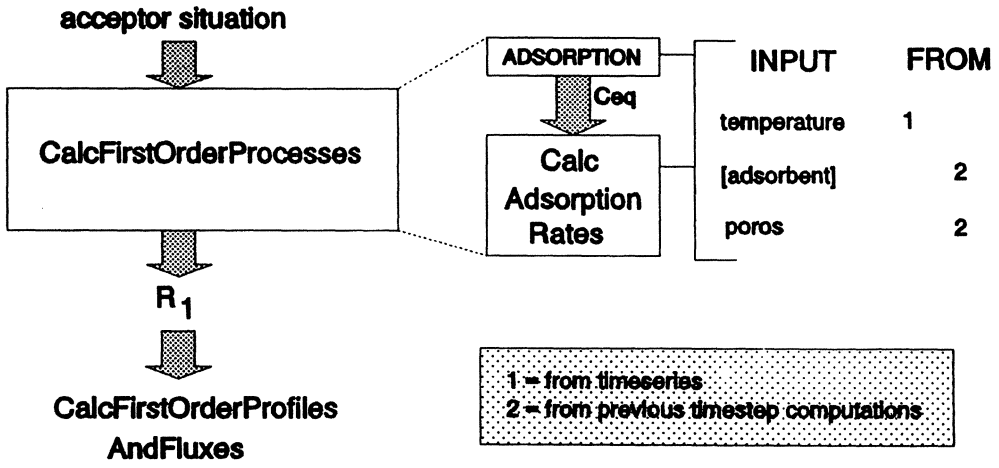


Figure 26. Calculation scheme for first order processes.

In Figure 24 a complete scheme is given showing the routine calling scheme in EcoWasp. The calculation of zero order and first order processes and the source of the necessary data is outlined in Figure 25 and Figure 26, respectively.

6. AUXILIARY PROCESSES AND CHARACTERISTICS; COMPUTATION TESTS

6.1. Bioturbation and bio-irrigation

Benthic animals enhance solid and liquid vertical transport which is referred to as bioturbation. Also, they may increase the exchange area of the sediment by constructing burrows and pumping overlying water through these burrows for their food supply or respiratory needs. Here, this is called bio-irrigation.

6.1.1. Bioturbation

The mixing effect of the bioturbation activity on solid distributions not directly influences pore water concentrations, and therefore, is not discussed here. When bioturbation also results in a transport of pore water, dissolved components may be imported from and into other layers. This is hardly to solve in a steady state profile computation as is implemented in EcoWasp. It would, for example, mean that there is some import of nitrate into a deep sediment layer. For simplicity we assume that this process is of limited influence. Part of the effects are included in the formulated description of the bio-irrigation process.

6.1.2. Bio-irrigation

Bio-irrigation is implemented as an increase of the effective diffusion coefficient of all dissolved compounds. Since the flux doubles when the exchange area is doubled, the effective diffusion coefficient has to be multiplied by four, in this case, because sqrt(D_{eff}) appears in all flux equations. Or

$$D'_{eff} = D_{eff} \cdot (\Delta\ Area)^2 \qquad (m^2 \cdot d^{-1}) \quad (68)$$

6.2. Temperature of the sediment layers

All the processes in the sediment depend on temperature. The formulation of this dependency is given in Brinkman (1993-b) and Brinkman and Smit (1993). The computation of the temperature profile is very straightforward: the temperature at the position ξ_{m+1} (m = the deepest sediment layer) is thought to be constant at 6°C. The temperature in the distinct layers are computed by linear interpolation between this standard temperature and the overlying water temperature T_0.

6.3. Influence of waves and currents in the overlying water on the sediment transport processes

Especially in relatively sandy sediments, waves and (tidal) currents may have large influence on pore water transport processes (e.g. Hüttel & Gust, 1992). Although the cause partly is a pore water current induced by pressure differences in the overlying water, we implemented the effect as an increase of the effective diffusion coefficient. Sediment constitution (sand, silt, clay) is an important parameter. The user has to assign a value to the relative increase of D_{eff} in each compartment, in each fixed layer. Thus,

$$D'_{eff} = D_{eff} \cdot (wave + current\ effect_{i,m}) \qquad (m^2 \cdot d^{-1}) \quad (69)$$

where i and m are compartment and fixed layer number, respectively.

6.4. Effect of sediment emersion

During periods of emersion, contact with the overlying water does not exist. In the case of oxygen, carbon dioxide and ammonia, exchange with the atmosphere might be of importance, although the atmosphere/water exchange is (much) slower than the sediment/water exchange. Other elements have no atmospheric exchange properties. It may be discussed whether these other components are exchanged proportionally to the submersion time or show such an enhanced exchange during submersion that, integrated over a tidal period, the total exchange is the same as it would have been under complete submersion. Probably both extremes are wrong, but regarding the steady state assumption, the second more convenient approach is applied in EcoWasp. For the elements with atmospheric exchange, it is assumed that during emersion, there is no flux from or into the overlying water, but from or into the air. For oxygen, ammonia and carbon dioxide the fluxes from and to the sediment do not change, but the effect on the overlying water is proportional to the length of the submersion period.

6.5. Computation tests

6.5.1. Computation of oxygen and nitrate penetration depths

For the western part of the Dutch Wadden Sea (see EON, 1988-a; 1988-b) a three year test simulation has been done. This western Wadden Sea is divided horizontally in twelve compartments (Figure 27). There is exchange between the Wadden Sea and the adjacent North Sea, extra inputs come from the fresh water Lake IJssel. Primary production results from flagellates, and pelagic and benthic diatoms. Oxygen, carbonate, nitrate, ammonium, phosphate and silicate are main dissolved inorganic compounds. A number of detritus types is distinguished. One benthic filter feeder is present. Weather data for 1987 are also used for the 1988 part of the simulation. The simulation concerns a validation simulation, describing field observations satisfactorily.

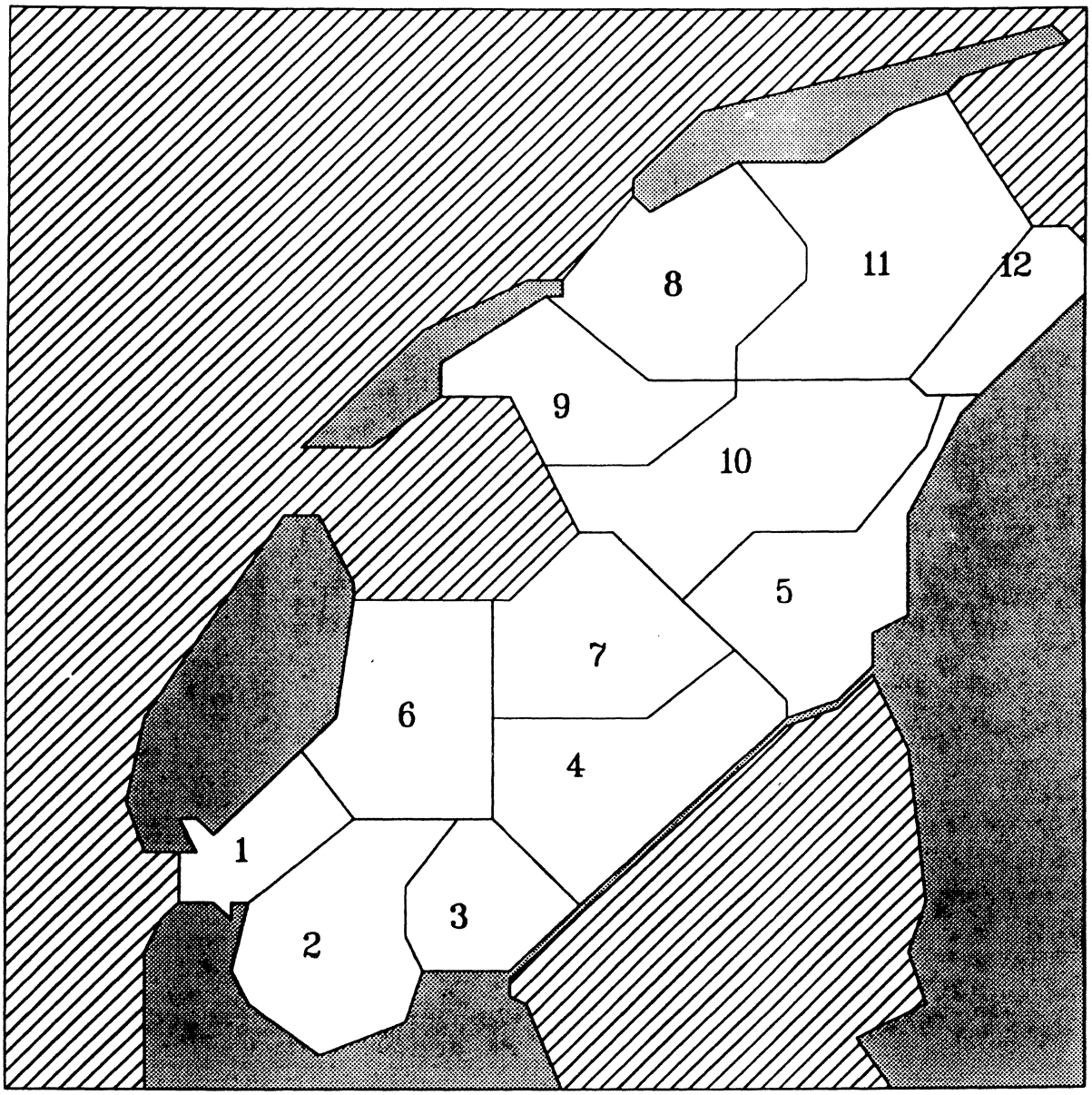


Figure 27. Compartments in the western Wadden Sea (according to EON, 1988-I).

In Figure 28 oxygen and nitrate penetration depths in the sediment of compartment 5, one of the more central compartments in the western Dutch Wadden Sea. In summer, when temperature and load of organic matter are high, the penetration depth is small (less than one centimetre). In winter, penetration depths increase as a result of a low organic matter supply and a low biochemical activity. For other compartments a similar result is found.

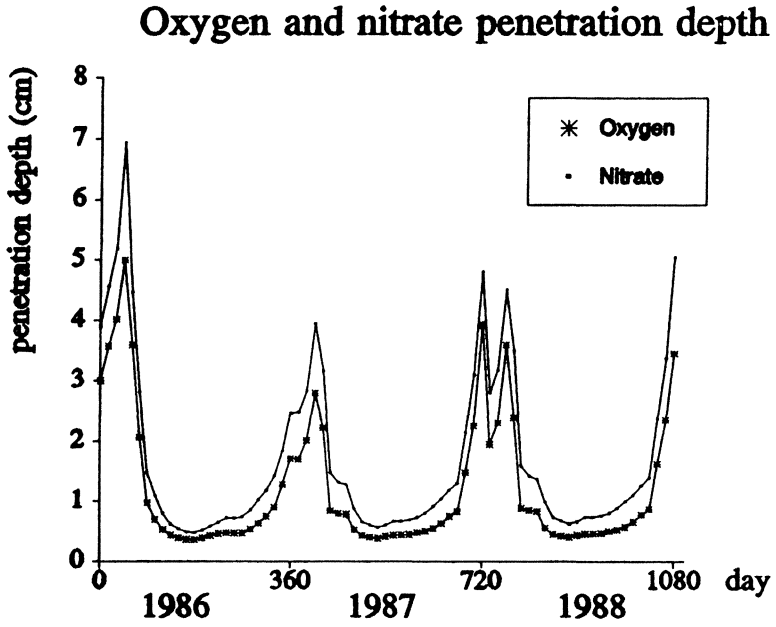
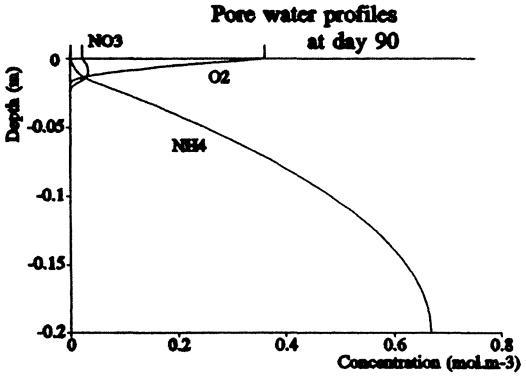


Figure 28. Oxygen and nitrate penetration depths for compartment 5 (EON, 1988-1) as computed by an EcoWasp test simulation. For 1988, data from 1987 have been used.



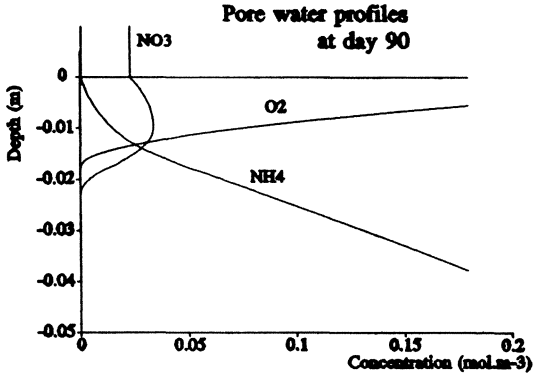


Figure 29. Pore water profiles as computed by an EcoWasp test simulation for compartment 5 in the western part of the Dutch Wadden Sea.

Figure 30. Pore water profiles as computed by an EcoWasp test simulation for compartment 5 in the western part of the Dutch Wadden Sea. Enlargement of Fig. 29.

6.5.2. Pore water profiles in some test situations

Pore water profiles for a test situation where nitrification is important are shown in Figure 29 and enlarged in Figure 30.

6.5.3. Fluxes in some test situations

In Figure 31 - Figure 35 fluxes of oxygen, nitrate, ammonia, phosphorus and silicate as computed by EcoWasp for this test simulation are shown. The tests show that the model outcomes are quite stable and do not diverge and do not strongly alternate. The absolute values of these fluxes should be comparable to the real fluxes in the Wadden Sea system, but the model is only 'calibrated' by eye. Mind that a positive flux is directed downwards.

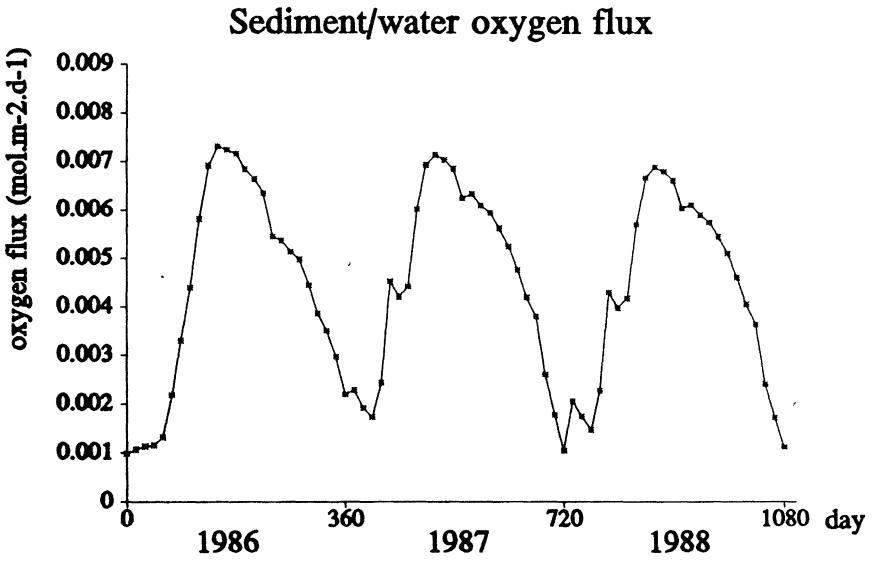


Figure 31. Oxygen fluxes through the sediment/water interface as computed by EcoWasp in a test simulation for the western part of the Dutch Wadden Sea.

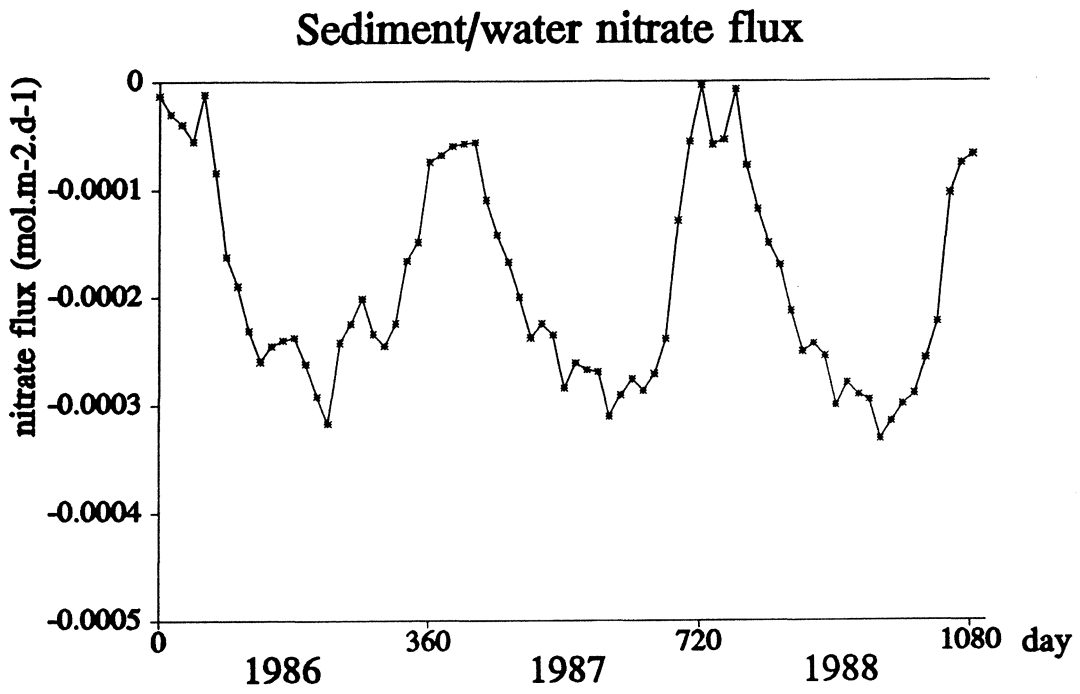


Figure 32. Nitrate fluxes through the sediment/water interface as computed by EcoWasp in a test simulation for the western part of the Dutch Wadden Sea.

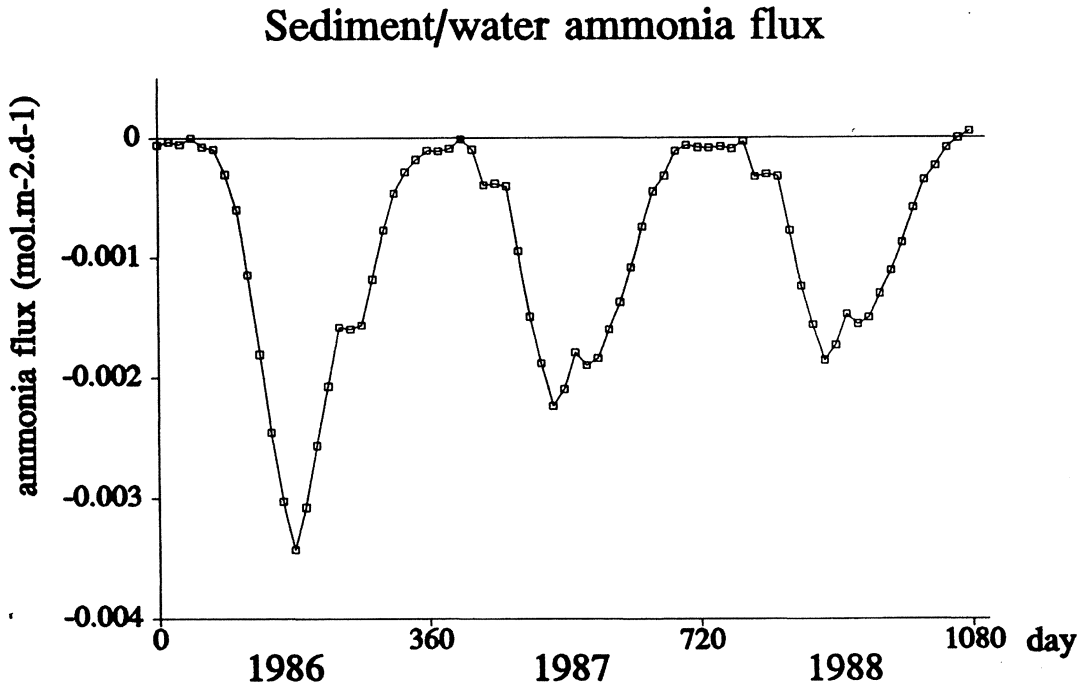


Figure 33. Ammonia fluxes through the sediment/water interface as computed by EcoWasp in a test simulation for the western part of the Dutch Wadden Sea.

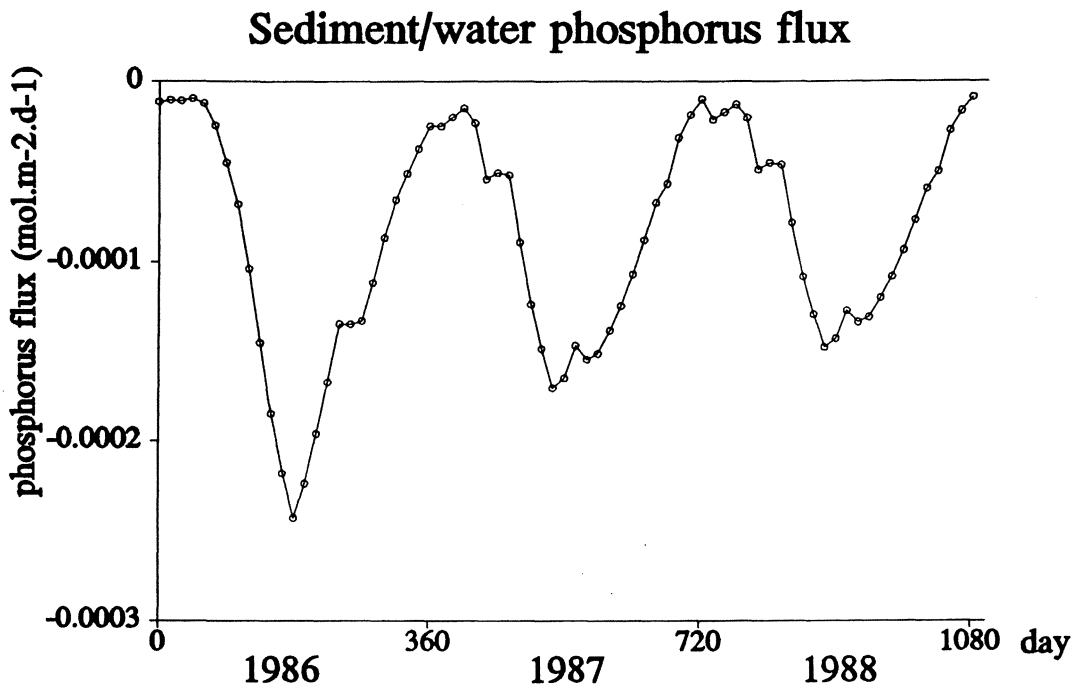


Figure 34. Phosphorus fluxes through the sediment/water interface as computed by EcoWasp in a test simulation for the western part of the Dutch Wadden Sea.

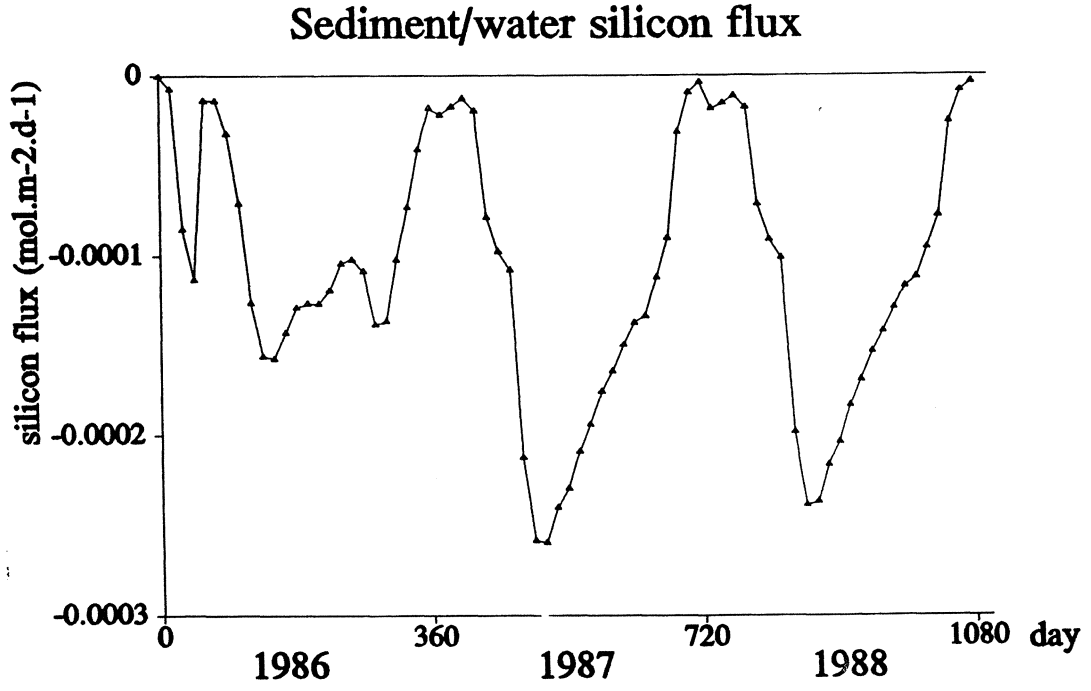


Figure 35. Silicon fluxes through the sediment/water interface as computed by EcoWasp in a test simulation for the western part of the Dutch Wadden Sea.

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Appendix 1 Computation of the penetration depth of an electron acceptor when more than one layer is involved

In section 3 the iterative procedure to find a best estimate for the pore water profiles is outlined. Part of that description concerned the computation of the penetration depth of an electron acceptor in the sediment. When the acceptor penetration depth in a layer j has to be computed, and this layer j is *not* the sediment toplayer, then an iterative routine is needed. It is mentioned that in such a case, the concentration $C_j(0)$ of the acceptor at the plane j between the layers (j-1) and j is the estimator. Here the algorithm of this iteration is treated in more detail.

The iteration is done in three subsequent steps starting with an estimate for the $C_j(0)$, which will be called $C(0)_{est}$. Then, the penetration depth into the layer j is computed, using eq.(29). Following the scheme in Fig.7, α-values are computed, and thus also $C_j(0)$: $C(0)_{calc}$. When this $C(0)_{calc} > C(0)_{est}$, then $C(0)_{est}$ is increased. This is repeated until $C(0)_{calc} < C(0)_{est}$. Now the upper and the lower limits of $C(0)_{est}$ are known. In the second stage, a weighted bisection procedure (Pegasus procedure, see Engeln-Müllges & Reutter, 1988) is used to narrow the range. Finally, a Newton procedure is applied to find an accurate value for $C(0)_{est}$. Usually, after two or three bisection computations and two or three Newton calls a relative accuracy of at least 10^{-6} is found.
This three stage procedure was necessary because a Newton procedure alone appeared to be unstable. The first two stages are needed to get a suitable first estimate for the Newton routine. The weighted bisection already gives an accurate estimate, but it approaches the best value more slowly than the Newton routine does.